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# SOIL SCIENCE

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## POTASSIUM SYMPOSIUM

This number of SOIL SCIENCE is devoted exclusively to 12 papers that were presented before the Division of Fertilizer Chemistry of the American Chemical Society at its annual meeting held at the Statler Hotel in Buffalo, New York, on Tuesday, September 8, 1942. The meeting was attended by over 100 chemists who are concerned with the problem of the use of potassium as a fertilizer element. The papers give a fairly complete picture of the current status of our knowledge on the soil-plant interrelationships of this element. We welcome the opportunity to present the papers of this symposium for the benefit of the readers of this Journal.

FIRMAN E. BEAR

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### POTASH FIXATION IN CORN BELT SOILS<sup>1</sup>

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*Illinois Agricultural Experiment Station*

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The word "fixation" has been a problem-child of soil scientists for many years. Perhaps its first use was in reference to nitrogen, following the famous discovery of Hellriegel and Willfarth. Nitrogen fixation is essentially a conversion of unusable nitrogen into forms usable not only by the host plant, but also, with fairly easy transformations, by plants growing subsequently. Its next use concerned phosphates. "Fixation," applied to phosphates, had the opposite meaning, namely, conversion to forms unavailable, or at least less available, to plants. But what does "unavailable" mean? Does it mean not absorbable by plants at once, or not readily changed into absorbable forms? Lacking a precise definition, quantitative determination of fixed phosphorus would be impossible. For purposes of measurement, therefore, "fixation of phosphorus" has been defined by some investigators as removal from aqueous solution. Inevitably the third member of the triumvirate arrived, and we now have "potash fixation." Like phosphorus fixation, "potassium fixation" has generally been conceived to mean conversion to unavailable or to less available forms.

Soil potassium exists in many forms. First, there is a limited amount of water-soluble potassium in the soil solution. Then there is a larger amount of instantly replaceable potassium associated with the colloidal clay and perhaps also with organic colloids. This form, though not appreciably mobile in the soil mass is generally conceded to be readily absorbed by plant roots that make contact with it. The terms "replaceable" and "available" have come to be syn-

<sup>1</sup> Contribution from department of agronomy, Agricultural Experiment Station, University of Illinois. Published with permission of the director of the experiment station.

<sup>2</sup> The authors are glad to acknowledge the financial assistance afforded through a grant from the American Potash Institute, Inc., which made possible the research on many phases of this problem.

onymous, therefore, in the minds of many soil investigators and agronomists. Nevertheless, in some publications "potassium fixation" has been defined as conversion from the water-soluble to the replaceable status. Next in order comes nonreplaceable colloid-held potassium, which can be removed to a greater or lesser extent by more rigorous means than ordinary salt leach and which under soil conditions is known to pass into the replaceable form. This colloid-held potassium, or at any rate a part of it, may thus be conceived of as difficultly replaceable. Finally, the bulk of the soil potassium is contained in primary minerals such as muscovite, biotite, and feldspars.

The present paper deals with but a small fraction of soil potassium, namely, the colloid-held potassium, both replaceable and nonreplaceable, and the interrelations between these forms. It is so restricted because colloid potassium is the portion of the total soil potassium chiefly concerned with supplying this element to crops both now and for many years to come in the climatic environment of the corn belt. The adequacy, conservation, and possible increase of colloid potassium are of great economic significance.

In this paper "potassium fixation" is defined as the change of water-soluble or replaceable potassium into forms that are neither water-soluble nor instantly replaceable. It is apparent that fixation of added potassium merely augments the supply of similarly combined K already present in ordinary soils. The amounts of nonreplaceable colloid potassium in soils are considerable, and widely variable, decreasing greatly in the most advanced stages of soil development. In a productive, dark-colored grassland soil for example, 5,300 pounds an acre, or 18 per cent of the total soil potassium, was found to occur as nonreplaceable colloid K. An old, worn, grassland planosol contained only about half as much, or 2,800 pounds an acre, which accounted for 11 per cent of the total K in that soil (7). The latter soil has long been seriously K-deficient for crop production; the former has grown large crops for many years and is not yet K-deficient or likely soon to be. The potassium fixed from additions cannot be distinguished by methods now known from similarly combined potassium naturally present in soil colloids.

#### THE SOILS STUDIED

In the present study surface soils from the plowed depth of six Illinois experiment fields were used. They represent a wide range of soil conditions such as is found in many parts of the corn belt. Numbers 1 to 4 on the map (fig. 1) are nearly level soils formed from loess. All except No. 4 developed under grassland conditions. Number 1 at Aledo is Sable silty clay loam, a dark-colored productive soil representative of stage 1 in development.<sup>3</sup> It is not potassium-deficient. Number 2 at Carlinville is Herrick silt loam, a grayish brown soil with tight clay B horizon, near stage 3 in development. It is somewhat deficient in potassium for high yields. Numbers 3 and 4 are very similar in characteristics, the former, Cisne silt loam, being a grassland soil, and the latter, Wynoose silt loam, having formed under timber vegetation. They are stage 5 in develop-

<sup>3</sup> This refers to the development-series of five stages established by R. S. Smith and E. A. Norton for Illinois soils formed from Peorian loess of varying thickness on Illinoian till.

ment, very old, poorly drained, with very heavy, impermeable B horizons, low in productive capacity and very deficient in potassium-supplying power. The soil of the Elizabethtown experiment field, No. 5, near the southern tip of the state is a reddish yellow silt loam, a worn hill soil, steep, and subject to serious erosion. The soil of the Dixon experiment field, No. 6, is undulating to rolling grassland silt loam consisting of a Muscatine-Tama association. The soil used in this study came from an area of Tama.

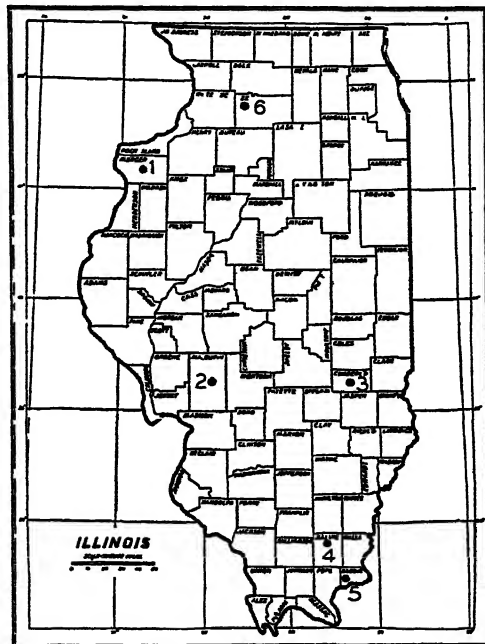


FIG. 1. SOIL EXPERIMENT FIELDS FROM WHICH SURFACE SOILS WERE TAKEN FOR POTASSIUM FIXATION INVESTIGATION

1. Aledo, Sable silty clay loam. 2. Carlinville, Herrick silt loam. 3. Toledo, Cisne silt loam (planosol). 4. Raleigh, Wynoose silt loam (planosol). 5. Elizabethtown, worn hill land. 6. Dixon, Tama silt loam.

#### METHODS

Several technics were used in these investigations, details of which will be mentioned in connection with individual projects. One of the principal methods involved prolonged storage of the moist soil alone and with varying concentrations of  $K_2HPO_4$  and  $KCl$  respectively. A 2-kgm. sample of the soil was stirred for 30 minutes with water or a solution of the respective salt (supplying up to 9,775 parts K per million of dry soil) at a semiliquid consistency. It was then dried at room temperature to optimum moisture for crop growth (40 to 50 per cent of water-holding capacity), screened, sealed in Mason jars, and stored at room temperature for periods of 2 months to 3 years. At the end of given periods aliquots were removed, dried at room temperature, and subjected to one or more of the following treatments: (a) Determination of replaceable K by ex-



haustive 0.5 N HAc leach for comparison of treated soils with untreated soils both before and after the moist storage; (b) extraction of residue from (a) by boiling in 1.0 N HNO<sub>3</sub>; and (c) alternate 0.5 N HAc leach and moist storage for successive periods of 30, 30, 90, and 90 days.

In another study extracted colloids fractionated into three size-grades were kept in moist contact with excess of K<sub>2</sub>HPO<sub>4</sub> and KCl respectively for a year, after which the increase in potassium soluble in 1 N and 5 N boiling HNO<sub>3</sub> was determined, as well as the gain in non-acid-soluble potassium.

#### RELEASE OF NATIVE SOIL POTASSIUM

At the outset, there is ample observational field evidence to establish the fact of release of soil potassium to the replaceable state. In the corn belt, rarely is more than a very few seasons' supply of replaceable K found in the root zone of either cropped or virgin soils. But many of the former soils have produced 50 to 75 good crops of corn and other grains, and promise to produce many more before a potassium deficit becomes evident. Whence can this K have come if not from nonreplaceable forms already in the soil? In 1932, biweekly measurements on the Ewing, Illinois, experiment field by the senior author showed a gradual drop amounting to 40 per cent of the replaceable K in the plowed depth from May to October, while a corn crop was growing, but the original level was regained by the next May. A similar observation was made by R. H. Bray<sup>4</sup> on the Dixon, Illinois, field with other crops. In another case a laboratory experiment was set up using eight widely divergent surface soils, which were held in moist storage for 6 months after exhaustive HCl leach and removal of the free acid. The results (3) showed a recovery ranging from 38 to 130 per cent of the initial K level. In five of the eight soils, the KCl fertilized plot of long standing gave a greater percentage recovery than the paired untreated one, in spite of the fact that the amounts of potassium applied were by no means sufficient to equal the K removal in the crops harvested.

When soils as taken from the field were kept under moist storage without previous removal of the replaceable K, little change occurred even in a long storage period (5 years), as is shown by Bray.<sup>5</sup> The shift was a release in some cases and fixation in others. These results suggested the existence of an equilibrium between the replaceable and nonreplaceable forms. Abel and Magistad's results (1) do not support the conception of a direct equilibrium for Hawaiian soils, because the gain in replaceable K was as great with fallowed soils as with those growing a succession of crops that removed much of the replaceable K as it was formed. There was no appreciable leaching loss in their experiments.

In order to examine the equilibrium possibility, Bray leached K-deficient and K-supplied soils respectively with H<sup>+</sup>, Ca<sup>++</sup>, and NH<sub>4</sub><sup>+</sup>, and then held them in moist storage for 6 months after adding increasing amounts of K<sub>2</sub>HPO<sub>4</sub>. His results<sup>6</sup> give good evidence of a state of equilibrium since, in both soils, fixation

<sup>4</sup> Unpublished work.

<sup>5</sup> Bray, R. H. The chemical nature of soil potassium in relation to its availability in Illinois soils. Doctorate thesis, Univ. of Illinois, 1940. [Unpublished.]

<sup>6</sup> *Ibid.*

occurred with high K applications and release with small or with no additions. These results also show that both the nature of the soil and the replacing ion, used for removing the initial replaceable K, influence the point at which the direction of the reaction is reversed.

Still another technic indicates that this is an equilibrium-reaction, so far as the soils studied are concerned. Soils of widely different origin and properties were heated in air at 200°C. for 6 days, during which twelve of them gained replaceable K while seven lost replaceable K (3, p. 104). These results indicate that not only does prolonged heating facilitate K fixation [as did also alternate wetting and drying by Volk (6), Page and Baver (5), and others], but that it also facilitates movement of K ions out of the fixed positions, the direction of the reaction again apparently depending on the balance between the two forms of potassium at the beginning of the heat treatment.

#### FIXATION OF ADDED SOLUBLE POTASSIUM BY DIFFERENT SOILS<sup>7</sup>

All the Illinois soils studied have been found to fix potassium in nonreplaceable forms, provided a sufficient concentration of K ion is brought into moist contact with them by addition as a soluble salt (table 1). The amounts fixed, as well as the addition required to bring about fixation, vary with different soils, depending presumably on the amounts of colloid in the different soils; on the particle size distribution, the potassium content, and the mineralogical constitution of the colloid; and perhaps on other factors. In most soils examined, the potassium extracted by 10 minutes' boiling in normal  $\text{HNO}_3$  was less than the amount previously fixed, provided again that a sufficient concentration of K ion was in contact with the soil during fixation. The 500 p.p.m. addition, for example, was not sufficient to increase the non-acid-soluble K in the Aledo soil, though it was sufficient in the other five soils reported in table 1.

The time required for the establishment of equilibrium between the different forms of soil K was studied with four of the six soils, by making determinations 8, 16, 25, and 52 weeks after additions of  $\text{K}_2\text{HPO}_4$ . The equilibrium was stable after 25 weeks in most cases. Table 2 illustrates one of these cases. The principal change between the sixteenth and the twenty-fifth week was the decline of acid-insoluble K from the peak value reached at 16 weeks to a level that remained constant after 25 weeks. This phenomenon occurred not only in the example given in table 2, but in 12 of 16 cases involving four different soils at four levels of potassium treatment. No explanation is offered. The only known environmental variation was that the laboratory temperature was somewhat lower during the first 16 weeks, ending the last of March, than during the next 8 weeks, which included the transition to summer laboratory temperatures.<sup>8</sup>

<sup>7</sup> In all the fixation studies hereafter reported, except as otherwise noted, K was added as  $\text{K}_2\text{HPO}_4$ . Also the soils were air-dried after the fixation period before the replaceable K was leached out. This method facilitated rapid leaching, but it was not adopted until comparative trials had shown that the amount of K replaced was essentially the same whether the soil was leached while moist or was first allowed to dry.

<sup>8</sup> Winter laboratory temperatures were approximately 65°F. at night and 75° during the day. Summer temperatures varied between about 80° and 95°.

The effect on fixation of increasing amounts of added potassium is illustrated in figure 2 for two different soil types. It will be noted that in Tama silt loam, a soil in early maturity and of fairly high productivity, the amounts fixed increased regularly with increasing additions. In contrast, the very old planosol, Cisne silt loam, fixed much less K, except at the highest concentration added, at which it fixed 43 per cent *more* K than Tama. The maximum addition, 9775 p.p.m.

TABLE 1  
*Fixation of potassium by different soils after addition of  $K_2HPO_4$*

SOIL	INITIAL K PRESENT		K ADDED AS $K_2HPO_4$	K PRESENT AFTER 1 YEAR'S MOIST STORAGE			
	Non- replaceable acid- soluble	Re- placeable		Replace- able	Acid- soluble	Gain in acid- insoluble	Total nonre- placeable
	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.
Aledo field, Sable silty clay loam.....	500	154	500	497	723	-56*	723
Carlville field, Herrick silt loam.....	273	42	500	203	318	294	612
Toledo field, Cisne silt loam.....	94	30	500	337	97	195	292
Raleigh field, Wynoose silt loam.....	84	64	500	256	181	211	392
Elizabethtown, worn hill land.....	251	58	500	214	430	165	595
Dixon field, Tama silt loam..	365	52	500	302	502	115	617

\* That is, 56 p.p.m. was released from acid-insoluble to acid-soluble, but still non-placeable, in the face of 500 p.p.m. addition on the soluble side of the equilibrium.

TABLE 2  
*Time required for potassium fixation equilibrium in Wynoose silt loam (Raleigh field)\**

TIME OF MOIST CONTACT	REPLACEABLE PLUS WATER-SOLUBLE POTASSIUM	ACID-SOLUBLE K	GAIN IN ACID-INSOLUBLE K
weeks	p.p.m.	p.p.m.	p.p.m.
0	564	84	0
8	327	179	142
16	269	132	247
25	272	160	216
52	256	181	211

\* Initial water-soluble plus replaceable K, 64 p.p.m.; 500 p.p.m. K added as  $K_2HPO_4$ .

amounted to one symmetry concentration in the Tama soil but was 2.6 symmetries in Cisne, so that the concentration with respect to the exchange capacity was much greater in the latter soil. These fixation curves indicate an adsorption type of reaction and they do not indicate that a definite maximum fixation capacity has yet been demonstrated in either soil. If all the fixed K atoms fell into the centers of the oxygen hexagons of the crystal lattices, as suggested by Page and Bayer (5), the fixation capacity would be definitely limited by the number of such spaces. But the K ions forced into such "fixed" positions in this

study may have been far short of such a maximum. The increasing amounts fixed with increasing additions, as well as the gradient in difficulty of removal, suggest that the K ions, whether or not they take the vacant positions in the oxygen layer, begin by taking places near the surfaces or edges of the particles, and they or succeeding ions penetrate to increasing distances between the lattice layers with increasing concentration of added K and with increasing time of contact. These observations do not controvert the possibility of complete penetration and the attainment of a definite maximum capacity if sufficiently rigorous and long-continued treatments were employed.

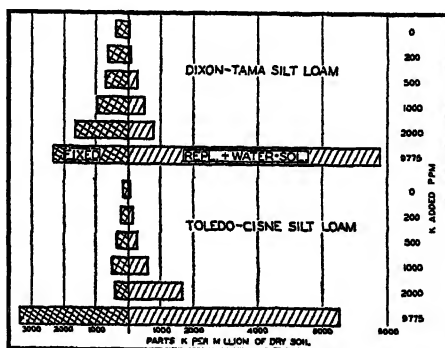


FIG. 2. AMOUNTS OF POTASSIUM FIXED DURING 1 YEAR BY TWO SOILS FOLLOWING ADDITION OF INCREASING AMOUNTS OF POTASSIUM AS  $K_2HPO_4$

Amounts in parts per million of dry soil

#### STATUS OF FIXED K

Another study has been started for the purpose of throwing more light on the status of fixed K. Only preliminary results have been obtained. One-micron colloid was removed from Tama silt loam and Cisne silt loam and fractionated into three sizes, i.e., 1 to 0.1, 0.1 to 0.06, and less than 0.06  $\mu$  effective diameter. Each sample was divided into three parts. One part was kept moist for a year with no treatment, another with an equal weight of K as  $K_2HPO_4$ , and a third with an equal weight of K as KCl. Then the replaceable K was removed with HAc and the residue digested 10 minutes in boiling  $N HNO_3$ . The residue from that digestion was similarly boiled in 5  $N HNO_3$ , and the last residue subjected to total K determination by fusion. Five-normal  $HNO_3$  was chosen for this extraction because previous trials on the whole soil using from  $N$  to 10  $N$  concentrations had shown that the K extracted leveled off at 5  $N$ . As the results are similar for the two soils, only those for Tama are given (fig. 3). The high potassium content of the coarse fraction indicates the illite nature of this colloid, as known from chemical, petrographic, and x-ray identification in similar soils (4). The superfine fraction is known to be chiefly a beidellite-like mineral on similar grounds (2).<sup>9</sup>

In all cases K fixation occurred. The gain in K soluble in normal  $HNO_3$  was

<sup>9</sup> Also unpublished work of R. E. Grim and R. H. Bray.

pronounced in all cases; that extracted by 5 *N*  $\text{HNO}_3$  was probably within the experimental error. Gains in acid-insoluble K were inconsistent, but notably large in two cases, namely 2.4 and 4.4 parts per thousand in the coarse and superfine colloid respectively, when added as the phosphate. Digestion in boiling 5 *N*  $\text{HNO}_3$  removed measurable amounts of Fe, Al, and  $\text{SiO}_2$  along with the K, a fact which suggests partial destruction of the colloid. Should this occur, the results of analysis of the residue would likewise be vitiated. Although this study of the separated colloid requires confirmation, it does afford convincing qualitative evidence of potassium fixation in colloidal particles of all sizes below  $1\ \mu$  and the evidence is equally convincing that the fixed K ions vary in status, i.e., in depth of penetration into the particle, in mode of attachment, or otherwise to account for the observed gradient in ease of removal.

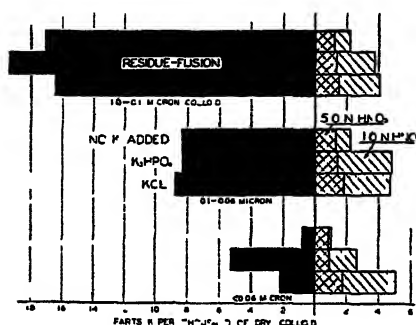


FIG. 3

FIG. 3. STATUS OF FIXED POTASSIUM IN COLLOID FROM TAMA SILT LOAM AFTER 1 YEAR'S MOIST CONTACT WITH AN EXCESS OF K ADDED AS  $\text{K}_2\text{HPO}_4$

Ratio: 1 gm. K to 1 gm. dry colloid equivalent

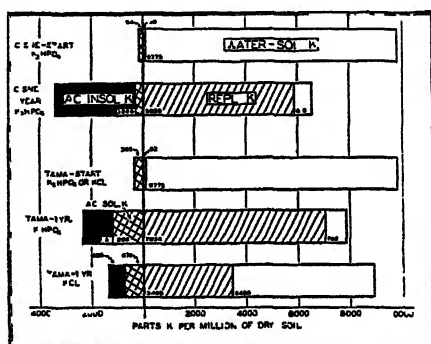


FIG. 4

FIG. 4. CONVERSION OF WATER-SOLUBLE POTASSIUM TO REPLACEABLE AND NONREPLACEABLE FORMS FOLLOWING ADDITION TO SOILS AS THE CHLORIDE AND THE PHOSPHATE

#### EFFECT OF ANION

The comparative effects of the  $\text{PO}_4$  and  $\text{Cl}$  anions on Tama silt loam whole soil were studied with 500 and 9,775 p.p.m. additions. Results of the latter are shown in figure 4. In this study the water-soluble and the replaceable K were separated by means of a preliminary 60 per cent MeOH leach. The relation between replaceable and water-soluble K is noteworthy. A large part of the water-soluble K (7,056 p.p.m.) was made replaceable when added as the phosphate, whereas more than half of that added as chloride (5,400 p.p.m.) remained water-soluble. This behavior may be explained by considering the  $\text{PO}_4$  ion as a link connecting some of the K ions to the colloid particle, in addition to adsorption of K by the usual mechanism. The  $\text{PO}_4$  ion is known to replace OH ions in the clay colloids. One, two, or all of the three oxygens of the OH groups attached to the P atom in  $\text{H}_3\text{PO}_4$  may be conceived as replacing OH groups in the surface or in the edge of the colloid particle, giving an Al-O-P linkage. Such an arrangement with three-point attachment would place the entire base of the  $\text{PO}_4$

tetrahedron in the colloid surface and could occur, if at all, only in a mineral like kaolinite in which a lattice surface consists of a layer of adjacent OH groups. One-point attachments are more to be expected in montmorillonitic clays in which the OH groups are farther apart. If only one OH is replaced, two negative charges are available on the  $\text{PO}_4$  to hold K ions, thus increasing the base-adsorbing capacity of the colloid without disturbing the normal base-exchange valences. If a two-point attachment of  $\text{PO}_4$  occurs, then one valence is added for K. Other factors conceivably might influence the manner of attachment of the phosphate to the colloid, such as the number of K ions or other cations in the solution competing for positions.

Actually, treatment of this soil for a year with  $\text{K}_2\text{HPO}_4$  increased its base-exchange capacity by several milliequivalents, as determined by the usual  $\text{NH}_4\text{Ac}$  leach, a fact which accords with the above explanation of phosphate effect.

It will be noted that association with the  $\text{PO}_4$  anion resulted in nearly doubling the amount of fixed K in both the acid-soluble and the acid-insoluble status, as compared to the chloride. It is not so easy to visualize the same type of mechanism for the interior of the colloid particle as is postulated for the surface reaction. However one visualizes the fixation mechanism, it may be conceived that the  $\text{PO}_4$  ion increases fixation by virtue of its increasing the replaceable K, i.e., increasing the concentration of K ions held in contact with the colloid surfaces.

It has been suggested by Volk (6) and others that potassium, on being fixed in soil colloids as a result of repeated wetting and drying at somewhat elevated temperatures, may assume the status of a mica-like mineral, and both Volk and Gieseking<sup>10</sup> have obtained confirmatory x-ray evidence. The authors have prepared no x-ray diffraction patterns of extracted colloids subsequently treated with K ion by moist contact but have photographed many such patterns of colloids extracted from soils after the latter had been subjected to moist K contact as previously described. The results were negative except in a very few cases where faint strengthening of mica lines was observed. It is evident, therefore, that fixation produced by the moist contact technic did not proceed as far toward formation of a mica as with the more rigorous treatment used by other workers.

#### RELEASE OF FIXED POTASSIUM

As previously mentioned, it is not feasible to consider release of K fixed by additions as such, because this potassium in being fixed is merged with other potassium already in the colloid, which, so far as we know, is present in the same kind of physicochemical relationship. It is possible, however, to determine the increase in amounts of K released after such fixation and also to determine when in successive release periods the cumulative potassium released equals or exceeds the amount that had been fixed.

Such determinations have been made on four soils after 3 years<sup>11</sup> of moist contact with K additions. After exhaustive 0.5 N HAc leach and removal of free acid by MeOH these soils were stored for five successive periods of 30, 30, 30, 90, and 90

<sup>10</sup> Gieseking, J. E. Agronomy Department, Univ. of Illinois, personal communication.

<sup>11</sup> See footnote, table 3.

days, with similar HAc and MeOH leach at the end of each period. The cumulative release of K during the 330 days is shown in table 3.

In general, the greater the amount of potassium added, the more was fixed; and as more was fixed, greater amounts were subsequently released. The gradient of release, however, was less than that of fixation, and therefore where the greatest amount had been fixed only a small percentage was released. Following the 200-pound addition, the amounts fixed and then released were about equal. With larger additions the release was always less than the amounts that had been fixed. Such fixation may represent a more rigorous removal of added K from circulation than the farmer wishes, but with very large applications it is certainly desirable that not all of it be available for the first few crops; otherwise, it might be susceptible to serious loss in drainage waters.

TABLE 3

*Potassium released during 330 days in five successive periods, after fixation by 3 years\*\* of moist contact*

K ADDED ( $K_2HPO_4$ )	POTASSIUM RELEASED			
	Aledo (Sable)	Carlinsville (Herrick)	Toledo (Cisne)	Dixon (Tama)
<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>
0	174	72	52	49
200	155	104	84	116
500	225	117	126	151
1000			147	144
2000			166	319
9775			258	532
500*				199
9775*				1075

\* KCl.

\*\* Two years for Toledo and Dixon.

A more optimistic point of view is to consider that in every case the build-up of colloid K (nonreplaceable) as a result of additions has increased the colloid K reserve and has also enabled the soil to deliver more potassium to the replaceable form in the first season (330 days) than was released in untreated soils. Thus the K-supplying power of the soil has been improved. Whether greater release will continue as a result of the gain in fixed K remains to be determined.

#### PRACTICAL AND ECONOMIC SIGNIFICANCE OF POTASSIUM FIXATION

From the practical and economic point of view two questions at once arise. The first is: What is the value of potassium that has been fixed in the soil? The preponderance of opinion among soils investigators until now has been that its value is greatly diminished by fixation, in some cases almost to the vanishing point. The reason for this judgment is that fixation interferes with the immediate utilization of potash fertilizers by crops. On the other hand, as has been found for Illinois soils, fixation occurs slowly enough that most of the potassium absorption by the current crop will have taken place before the maximum fixation

is accomplished, especially if the potassium is applied by the hill or row method, and thus interference with plant absorption during the season of application may not be of major importance in corn belt soils. Not all of a potash application is ordinarily taken up by the first crop, and fixation, as well as conversion to the replaceable status, decreases the loss of unused potassium in drainage water. As to what proportion, if any, of the potassium fixed is permanently removed from the possibility of crop utilization, nothing final can be said. Certainly, the Illinois studies to date show that amounts significant in crop growth can be recovered the first year after a 3-year fixation period. There appears no reason to doubt a smaller but still significant release in subsequent years. It is probable that potassium fixation has been a more serious handicap in crop utilization from fertilizer applications in other regions than in the corn belt; and it is likewise possible that fixation in corn belt soils may be more serious in dry seasons than was the case in these studies, in which the soils were kept continually moist.

The protection against leaching loss by fixation following large potash applications, which are now of considerable interest, is a certainty; and the studies here reported indicate that such additions result in a build-up of the colloid-held potassium reserve, which is the reservoir from which supplies of available K for crop production are derived year by year. Large potash fertilizer additions should thus be expected to lengthen the potassium-supplying life of the soil.

This interest in large potash applications leads to the second question: Will the leaching losses incident to such additions result in so great a wastage before fixation becomes effective as to preclude this method of using potash fertilizers? We shall not attempt an answer at this time. Two observations have been made, however, which have a bearing on the question. Three years ago additions of KCl were made in the field at the rates of 1, 2, 4, 8, and 20 tons an acre. Qualitative tests show that during the 3 years vertical penetration and accumulation have occurred at least to the B horizon, and laterally for several feet. No plants grew after the 20-ton dosage for 2 years, but in the third season the best looking oats in the field grew on this area. The grain yield equaled that in the rest of the field. The second observation was made on lysimeters 1/1200-acre in area and 5 feet deep in which corn was grown. Additions of KCl and of  $K_2HPO_4$  were made 18 months ago at the rate of 1 ton an acre. During the first 12 months, with runoff prevented by walls extended above the surface, no excess potassium appeared in the drainage water as compared to untreated tanks, but large increases were found in the drainage loss of calcium and magnesium. These observations do not suggest a likelihood of serious potassium leaching losses from heavy dosages.

#### SUMMARY

A study of the results of investigations herein reported with Illinois soils and of work by other investigators leads to the belief that potassium fixation is well-nigh universal in the soils of the corn belt when soluble potassium salts are added.

It has been found to occur gradually under moist storage conditions, reaching equilibrium in about 6 months. Evidence submitted supports the theory that fixed potassium is in equilibrium with that in the replaceable status, since the



reaction can be made to go in either direction by altering the concentration relations. Significant release to the replaceable form has been attained within 30 days under conditions of nonequilibrium favorable to release (removal of replaceable K). The amounts so released in 330 days were greater in soils that had been allowed to fix K from additions than in untreated soils. Although recovery of amounts equal to the quantity previously fixed has not yet been attained where the amounts fixed were large, it is reasonable to expect that this will be accomplished with sufficient time.

The amount of potassium fixed after uniform additions varies with different soils, but no precise correlation has been established between the amounts fixed and base-exchange capacity or any other soil characteristic. No maximum limit of fixation capacity has been demonstrated by means of additions up to 10,000 p.p.m., equivalent to 20 tons of KCl an acre.

Addition of potassium as the phosphate results in greater K fixation than addition of equivalent amounts as the chloride, and also results in a higher ratio of replaceable to water-soluble K. The latter phenomenon is explained as probably due to  $\text{PO}_4$ 's serving as a link between K ion and colloid particle, by replacing one or two OH ions in the latter for each  $\text{PO}_4$  ion adsorbed.

Significant amounts of K were found to be fixed by extracted soil colloids of three different particle size grades, all less than  $1\mu$  in effective diameter. Some of the potassium thus fixed was not extracted by boiling in 5 N  $\text{HNO}_3$ .

Potassium fixed from additions is considered as an addition to similar forms already present in the soil colloids, which are the reservoir for year by year renewal of replaceable potassium following its removal in crops and drainage water.

Although fixation may interfere with immediate crop utilization of potassium added in fertilizers, it retards wastage by leaching and adds to the natural reserve of soil colloid potassium which is partly recoverable in a few weeks and perhaps completely so in a longer time. These results afford evidence that potassium fixation in corn belt soils has merits which counterbalance in considerable measure its recognized disadvantages.

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# POTASSIUM IN THE SOIL COLLOID COMPLEX AND PLANT NUTRITION<sup>1</sup>

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Carbohydrate formation is the particular role commonly assigned to potassium. This does not deny possible precursor service in the production of proteins, when these bear close structural resemblance to carbohydrates. The specific performances of potassium, however, are still enshrouded in mystery. With fuller understanding of the behavior of nutrient elements in the soil there is hope of elucidating potassium performances in both soil and plant. It was through the use of colloidal clay as a growth medium, that the concepts reported in this paper regarding potassium were formulated.

## RELATION OF SOIL DEVELOPMENT TO POTASSIUM OF COLLOID

Potassium makes up a part of the crystal structure of colloidal clay. It is also adsorbed on the clay surface in a mobile form. In the beidellitic clay of Putnam silt loam, more particularly the fraction consisting of electrodyalyzed particles with maximum dimensions of  $0.2 \mu$ , the potassium within the crystal comprises less than 1 per cent,<sup>2</sup> whereas that in the adsorbed form may be as much as 2.535 per cent of the weight of the clay, of which the exchange capacity is 65 m.e. per 100 gm. As this clay occurs naturally in the soil, however, only a small portion of the exchange capacity is taken by potassium. The maximum is usually 0.1 per cent of the weight of the clay, or less than 5 per cent of its capacity.

Magnesium stands next to potassium in amount within this colloid crystal. It is also low in the exchangeable form.<sup>3</sup> Within the crystal, calcium is less than one fifth of the potassium. In their exchangeable forms, however, the calcium may be 10 times as great as the potassium.

These relations vary within different soils under different degrees of development. It is because of the resulting changes in the clay crystal, in the adsorbed nutrient cations, and in the accompanying amounts of the adsorbed nonnutrient hydrogen, that the soil may control both the kind and the amount of vegetation.

Potassium behavior on the colloidal clay, even when this is isolated from the other separates of the soil, is complicated by the fact that the clay varies in its crystal composition and in its exchange capacities and components, as a consequence of the climatic and other factors that produced it. The parent material of the clay is apparently not a significant determinant.

Analyses by Brown and Byers (4) of eight colloids from the B<sub>1</sub> horizons of eight different soils of granitic origin in the humid region under variable temperature on

<sup>1</sup> Contribution from the department of soil, Missouri Agricultural Experiment Station, Journal Series No. 865.

<sup>2</sup> See analyses by Marshall (11) and by Ferguson (5).

<sup>3</sup> Unpublished data of E. O. McLean and W. J. Pettijohn.

the eastern slope of the Appalachians showed that  $K_2O$  ranged from 0.14 to 1.58 per cent,  $CaO$  from 0.04 to 0.75 per cent, and  $MgO$  from 0.07 to 1.36 per cent. In only one case was the amount of potassium less than that of calcium. Similar studies of nine colloids in  $B_1$  horizons from limestone valleys in eastern United States by Alexander *et al.* (3) showed that  $K_2O$  ranged from 0.15 to 2.30 per cent,  $CaO$  from 0.10 to 0.77 per cent, and  $MgO$  from 0.49 to 2.18 per cent. In each case the potassium content was higher than the calcium. In a tenth case all three constituents were high, and the calcium was higher than the potassium. These two studies point to dominance of potassium over calcium in the colloids in well-developed soils, whether of granitic or limestone origin.

In some so-called "very young" soils in the Hawaiian Islands, Hough *et al.* (8) report eight of nine colloids higher in calcium than in potassium. In so-called "older" soils from similar parent materials, three of five had more potassium than calcium in their colloids. This suggests, in agreement with the other analyses, that weathering under higher rainfall gives colloids of higher potassium than calcium content, whereas under lower rainfalls calcium may dominate over potassium in the "younger" colloids. The potassium content in the crystal of the colloid may, then, be mainly a matter of climatic origin.

In a recent study (13) of the clay fraction of the loessial soils of central United States so selected as to maintain all other factors in soil development constant while rainfall and temperature increased, it was clearly demonstrated that potassium behavior must be viewed in relation to several variables affecting both the colloidal clay and the plant nutrients derived from it. This is illustrated by the data in table 1 for four loessial profiles of silt loam in different locations extending through rainfall increase from 27 to 55 inches. The temperature increase in these four locations was from 8.72 to 17.66°C.

With increasing rainfall and temperature, the nature of the clay changed markedly as its silica-sesquioxide ratio narrowed from 5.06 to 2.56, and its exchange capacity decreased from 73 to 44 m.e. per 100 gm. of clay in the B horizon. At the same time potassium, in general, occupied an increasingly smaller percentage of the exchange capacity. Since at Sioux City, Iowa, the potassium saturation was only about 2.5 per cent, its reduction to less than 1.5 per cent at Wickliffe, Kentucky, with an increase in rainfall of 21 inches means decidedly reduced supplies of available potassium for plants. These facts indicate that there is cause for concern about potassium for crops when the exchangeable supply is no larger than 100 pounds per 2,000,000 of soil, as in these more highly weathered soils. The weathering forces are reflected in the composition of the clay they produce.

#### RELATION OF POTASSIUM TO OTHER CATIONS ON THE SOIL COLLOID

Although the soils under study showed decreasing amounts of both exchangeable potassium and calcium with increase in weathering, the decrease in calcium was at a much greater rate. This is shown in table 1 by the calcium-potassium ratio. For each of the three horizons in the solum, this became smaller as the location of the sample moved southward into higher temperature and rainfall.

These facts suggest that differences in total exchangeable potassium alone

would be a less reliable index of soil productivity than the relation of potassium to other nutrients. Such a relation would appear to be a potent factor in determining the kind of vegetation a soil will support.

Magnesium in its relation to potassium, in table 1, is also of interest. In their exchangeable amounts, these two cations decline at similar rates with increasing intensity of climate, since the ratios for the corresponding horizons of the solum are not significantly different in the locations other than Sioux City. This suggests that magnesium and potassium are weathered out as exchangeable forms at about the same rate. It suggests further, that the ratio of calcium to magnesium

TABLE 1

*Some ratios of exchangeable cations and other properties of colloids in soils developed from similar parent materials under different climates*

LOCATION	ANNUAL RAINFALL	HORIZON*	EXCHANGE CAPACITY†	SiO <sub>2</sub> R <sub>2</sub> O <sub>3</sub>	Ca† K	Mg† K	Ca† Mg
	<i>inches</i>		<i>m.e./100 gm.</i>				
Sioux City, Iowa	27	A	73	5.06	64.3	7.7	8.2
		B			132.8	16.5	8.0
		C			177.2	29.4	5.9
		D			205.6	39.3	5.2
McBaine, Missouri	40	A	66	4.03	37.2	14.0	2.6
		B			33.0	13.4	2.4
		C			61.7	22.4	2.7
		D			51.9	23.0	2.2
Wickliffe, Kentucky	48	A	50	3.24	29.0	18.3	1.6
		B			24.2	24.7	0.95
		C			33.3	27.2	1.6
		D			121.1	84.6	1.4
Vicksburg, Missis- sippi	55	A	44	2.56	24.5	12.0	1.0
		B			15.8	14.0	1.1
		C			18.7	20.6	0.91
		D			186.1	96.4	1.9

\* A = 0-7 inches, B = 12-20 inches, C = 36-48 inches, D = 15-20 feet.

† This determination was made on the B horizon only.

‡ Calculated on basis of milligram equivalents, rather than weight equivalents.

on the colloid, like that of calcium to potassium, might be used as an index of soil development and productivity. The data for the former ratio (table 1) are of small range, however, and therefore not so revealing of differences as the values for the latter.

#### INFLUENCE OF POTASSIUM-CALCIUM RATIO OF COLLOID ON PLANT COMPOSITION

The behavior of potassium in the clay colloid, as revealed by chemical analyses and treatments, must be reconciled with its behavior in the plant. Potassium is lower than calcium in exchangeable form on the soil colloid, yet the former makes up 1.68 per cent in plants in contrast to 0.62 per cent for calcium as averages (15).

In view of the shifting ratios of these two exchangeable nutrients on the colloid with increasing degree of soil development, the question arises whether vegetation reflects corresponding differences in composition. As a test, chemical analyses of different crops (14) were assembled. The different crops were allocated according to dominance on (a) slightly developed, (b) moderately developed, and (c) highly developed soils. Though the numbers of cases are not extensive enough to warrant unqualified conclusions, they are suggestive, as presented in table 2.

The data show that the increasing degree of soil development, which gives decreasing calcium in relation to potassium on the colloid clay, gives correspondingly increasing potassium over calcium in the plant composition. Plants are lower in percentages of both potassium and calcium as the soil is more highly developed, but the potassium content drops to about one half while the calcium

TABLE 2  
*Composition of plants according to the degree of soil development*

	PLANTS GROWING NATURALLY ON SOIL DEVELOPED		
	Slightly, 38 cases	Moderately, 31 cases	Highly, 21 cases
Dry matter contents as			
K <sub>2</sub> O.....per cent	2.44	2.08	1.27
CaO.....per cent	1.92	1.17	0.28
P <sub>2</sub> O <sub>5</sub> .....per cent	0.78	0.69	0.42
Combined.....per cent	5.14	3.94	1.97
Amounts relative to highly developed soil			
K <sub>2</sub> O.....	1.9	1.6	1.0
CaO.....	6.8	4.1	1.0
P <sub>2</sub> O <sub>5</sub> .....	1.9	1.6	1.0
Ratios			
K <sub>2</sub> O:CaO.....	1.2	1.8	4.5
K <sub>2</sub> O:P <sub>2</sub> O <sub>5</sub> .....	3.0	3.0	3.0
CaO:P <sub>2</sub> O <sub>5</sub> .....	2.4	1.6	0.66

drops to about one seventh in going from slightly developed to highly developed soils. At the same time, the combined percentages of potassium, calcium, and phosphorus drop to two fifths. The ratio of phosphorus to potassium in the vegetation was constant.

If these are the facts in general for the assay of the soil by means of vegetation, it would seem that, among the plant nutrients on the colloid, potassium moves most actively into vegetation as the soil is more highly developed.

In previous experiments (6) soybeans were grown on colloidal clay supplied with exchangeable calcium and potassium in different ratios, but with constant supplies of calcium, nitrogen, and phosphorus, to determine whether the varying ratios influence plant composition. The results demonstrated that the increase of potassium relative to calcium increased the vegetative yield; reduced both the percentages and the totals of nitrogen, of phosphorus, and of calcium in the

vegetation; and increased both the percentage and the total of potassium according to the variable supply offered. All these characteristics suggest a crop of more proteinaceous nature containing higher concentrations of calcium and phosphorus when calcium dominates on the colloid, and of a more carbonaceous nature when potassium is high relative to calcium.

As a further test of the hypothesis, soybeans were grown similarly but for three successive crops in order to exhaust the soil fertility (5). The carbonaceous phases of the plants were separated into sugars, starch, and hemicellulose. In the first crop, nodule bacteria were withheld and the soybeans were grown as a nonlegume. The second and third crops were nodulated and behaved as legumes.

The results showed that in the first, or nonlegume, crop the total sugars were low and decreased in concentration while the vegetative yield was increasing with the increasing ratio of potassium to calcium. More noticeable, however, was the behavior of the starch, the concentration of which almost doubled and the total almost trebled with increasing potassium. When the same kind of plants behaved as legumes, their sugar concentrations were much higher and again suggested decrease with extra potassium. The starch concentrations were lower than those for the nonlegume, but increased for increments of potassium initially put on the colloid. The greater exhaustion of nutrients from the colloid by the third crop indicated that lowered soil fertility, like excessive potassium in relation to calcium, gave dominance to the carbonaceous character of the crop, as shown by the higher sugar and starch contents in the latter of the two leguminous crops.

The hypothesis that relative calcium reduction in the soil tends to reduce the proteinaceous nature of the vegetation is further supported by the decreasing protein content of wheat in going from west to east in Kansas, as reported for 1940 (10). Between western Kansas, with an annual rainfall of 17 inches, and eastern Kansas, with 37 inches, the protein in the wheat dropped from 18 to 11 per cent. This traverse represents a distinct change in the original grass vegetation (12) and a reduction in the amount of calcium in the soil, the calcium carbonate being at greater depths in the profile (9, pp. 122-123).

Still further support of the hypothesis is given by the recent studies of Allen<sup>4</sup> with percolating nutrient solutions for soybeans, and of Converse *et al.*,<sup>5</sup> with colloidal nutrient media for corn. Both show the association of the calcium-potassium ratio with protein content, whether the crop was legume or nonlegume.

Although calcium and potassium are seemingly reciprocals in plant composition, calcium supporting the proteinaceous and potassium the carbonaceous properties, there is a question whether the high level of phosphorus associated with the former and its low level with the latter are not involved. Apparently the phosphorus level deserves attention in connection with this ratio.

<sup>4</sup> Allen, D. I. Differential growth response of certain varieties of soybeans to varied mineral nutrient conditions. Doctoral thesis, University of Missouri, Columbia, 1942. [Unpublished.]

<sup>5</sup> Converse, J. D., Gammon, N., and Sayre, J. D. The use of ion exchange materials in studies on corn nutrition. [Unpublished.]

## MOVEMENT OF CATIONS BETWEEN SOIL AND PLANT

If, on well-developed soils, potassium dominates the activities within the vegetation—for any form of which a carbonaceous skeletal structure is requisite—then the universal presence in soils of this nutrient in active form must be demonstrated. Chemical breakdown of the clay to deliver potassium is of no significance in providing active potassium (1). It must, therefore, be either the adsorbed potassium, or that provided by the breakdown of the mineral silt and sand separates of the soil, that serves. Plant growth may return potassium to the soil in temporarily mobile form, since this nutrient may go not only from the colloid clay to the plant, but also in the reverse direction during plant growth. Phosphorus and nitrogen have been found to return similarly. To date, calcium has been found to go only from the clay to the plant. Magnesium behaves much like calcium. The facts that potassium may be leached back to the soil by rain

TABLE 3

*Increase in potassium-saturation of colloid at low levels and decrease at high levels during growth of soybean forage*

CULTURE NUMBER	NUTRIENTS SUPPLIED*			YIELDS†, THREE CROPS	REMNANT POTASSIUM IN CULTURE			PERCENTAGE OF POTASSIUM "FIXED"		SATURATION EQUIVALENT OF REMNANT	
	Ca	K	Seed K		Total‡	Ex- change- able	"Fixed"	Initial	Remnant	"Fixed"	Ex- change able
	m.e.	m.e.	m.e.	gm.	m.e.	m.e.	m.e.			per cent	per cent
1	10	0	13.84	37.122	5.23	0.99	4.24	30.6	81.0	14.1	3 3
2	10	5	13.84	42.057	5.41	1.49	3.92	20.8	72.5	13.0	4.6
3	10	10	13.84	48.390	6.23	1.50	4.73	19.8	75.9	15.7	5.0
4	10	15	13.84	46.247	7.35	1.90	5.45	18.8	74.2	18.1	6.3

\* Other nutrients were adsorbed as constant amounts.

† Separate crop yields are given elsewhere (5).

‡ Calculated from potassium supplied and removed in crops. No leaching loss was possible.

from the above-ground parts of more mature plants, that it goes back via roots, and that it dominates all cations in plant composition, emphasize its nomadic nature, which hinders our understanding of its performances.

Recent studies (5) suggest that vegetative growth tends to maintain an equilibrium level of potassium in the clay. Data are given in table 3 which show that the soil originally without exchangeable potassium acquired this nutrient during the growth of soybeans while other nutrients were being exhausted to the extent that nitrogen fixation was prevented. In spite of this exhaustion, the plants still produced appreciable yields of dry matter and were higher in carbohydrates relative to protein than is common for this legume.

Nutrient shortage in the soil apparently may reduce protein manufacture in the plant severely but allow carbohydrate production at a liberal rate, even when losses of potassium from the plant to the soil are sufficient to lower the crop content below that in the planted seed. The trials indicated that this returning

potassium became temporarily nonexchangeable. The amount of the potassium initially active (seed and supplied) that became "fixed" was relatively constant (5.23-7.35 m.e.). This "fixation" is a function, apparently, of the amount of potassium rather than of the amount of the clay, as shown by the saturation equivalent of the remnant which increased in both the fixed and the exchangeable forms. For the three cultures to which potassium was supplied in addition to that in the seed, the ratio between these two parts of the remnant remained fairly constant as they both increased. It is this mobility and these differences in exchangeability that must be understood before chemical tests of potassium in the soil can be interpreted in terms of crop results.

Other aspects of potassium must eventually be given consideration. The interaction between the hydrogen colloid of the soil and the potassium-bearing minerals in the coarse soil separates serves to buffer the colloid with respect to potassium saturation. The universal occurrence of potash minerals in silts and sands, from which the exhausted colloid may obtain exchangeable or "fixed" potassium, as Graham (7) has demonstrated for calcium, complicates the matter. Then, too, the degree of hydrogen-ion saturation that is a helpful factor in mobilizing calcium, magnesium, and some other cations into plants (2) is apparently not so effective on potassium. It is possible that potassium may be adsorbed on the colloid with so much less force than some other nutrients that the presence or absence of hydrogen does not significantly alter its relative place in the lyotropic series. This would leave potassium undisturbed by the degree of soil acidity and would help to explain why potassium nutrition in plants does not fit into the concepts for other nutrients centered about soil acidity.

Another aspect warranting attention is the apparent association of potassium and silica in plants on certain soils. Although silica is the reciprocal of calcium, silica and potassium seemingly rise and fall together to a degree that is somewhat modified by amounts of potassium, phosphorus, and acidity in the soil. The degree of soil development and the kind of vegetation associated with it are apparently reflected in this potassium-silica partnership, much as in the calcium-potassium ratio.

Although the calcium-potassium ratio has been emphasized as a reflection, via the plant, of these nutrients on the colloid complex and in the soil mineral reserve, one must not deduce physiological functions to the extent of exclusion of one by the other. Before any plant can grow, it must have both calcium and potassium. At starvation levels and even at more nearly balanced concentrations, calcium and potassium are directly associated, and either one may be instrumental in moving the other into the crop.

In considering these many phases of potassium independently, one must be cautious about interpreting plant growth on the basis of any single-factor behavior. Interactions of factors are usually quite different from the sums of their individual effects. Plant growth is the result of numerous factors, the possible interactions of which may be legion. The interpretation of these interactions calls for more delicate tests than are commonly used. There is



some hope that animal assays of the crop may demonstrate that potassium is a soil factor that modifies the feeding value of forages.

The agricultural use of potassium may receive more attention in the future, not so much because the supply in the soil has declined suddenly, but because the supplies of calcium and phosphorus have suddenly risen through their stimulated applications as soil-conserving measures. Potassium may become more widely appreciated as a hidden deficiency by contrast through legumes producing heavily under calcium and phosphorus stimulation. This deficiency may not express itself immediately in the form of decreased tonnages of non-legume crops, but may be reflected in nutritional disasters through consumption of cereals and nonlegumes grown in exaggerated legume-soil-building programs. Calcium and phosphorus are necessary to guarantee the nutritious, body-building values of leguminous forages, but the question arises whether this fertilizer combination will make cereals equally as valuable as energy suppliers in animal nutrition. This question must be answered in the negative, if the calcium-potassium hypothesis in the ecological picture has good foundation. For cereals in the agricultural program, including graminæ, and all their uses in general, the potassium supply may well be liberal in relation to calcium, whereas for legumes the reverse seems to be demanded. Concern about potassium may well arise while legumes and nitrogen fixation are carrying enthusiasm for calcium and phosphorus as soil treatments to unusual heights.

#### SUMMARY

Degree of soil development is reflected not only in the amounts of potassium in the colloid crystal and in the adsorbed form, but also in its ratios to other adsorbed plant nutrients. For some nutrients the ratios are inverse, and for others direct. These ratios are reflected in plant composition, and the calcium-potassium ratio is suggested as a basis for ecological plant array. Differences in soil development apparently determine whether the vegetation will be chiefly proteinaceous or carbonaceous. Because of the prevalence of its minerals in the lithosphere, of its readily soluble nature, of its readiness to become insoluble and inexchangeable from the colloid, of its movement from vegetation to the soil through leaching from the tops or exchange from the roots, and of its reserve in the silt and sand minerals to buffer the clay, potassium is so nomadic that its performances in any particular situation are difficult to interpret. Apparently potassium is almost uninfluenced by the hydrogen ion that mobilizes other cations into plants. Its adsorbed form becomes "fixed" to a significant extent even during short periods of plant growth. It manifests many and varied chemical aspects in connection with the soil colloid. There is the hope, nevertheless, that when more of the possibilities for potassium outgo from and income to the colloid have been quantitatively evaluated, its behavior on the colloid complex and its service in plant nutrition may be better understood.

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# POTASSIUM ABSORPTION BY PLANTS AS AFFECTED BY CATIONIC RELATIONSHIPS<sup>1</sup>

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The ability of a plant to obtain sufficient amounts of K or other nutrient element for optimum growth depends not only on the concentration of the element in the nutrient medium in available form but also on certain environmental factors affecting its absorption. Among the environmental factors that have been studied is the concentration of other ions in the nutrient medium.

It has long been known that the presence of a large concentration of any cation in the nutrient solution results in decreased plant growth and that this so-called toxic effect of nutrient ions can often be overcome by increasing the concentration of another nutrient cation, thus providing a better balance between the ions in solution. Although no entirely satisfactory explanation has been offered for these results, plant analysis data have led to the theory that ions present in very high concentration in the nutrient medium depress the absorption of other ions of like charge, and may cause a deficiency of the latter for optimum plant growth. This theory in various modified forms has been referred to as the theory of ion antagonism.

Although considerable work has been done on the proper ratio of K to other elements in solution for optimum plant growth, much of it is difficult to interpret. As with most investigations of soil-plant relationships, those concerning the effect of different cations on K absorption by plants have been studied by means of both soils and solution cultures. Each of these general methods of approach has its definite shortcomings. In soil culture studies it is often difficult to separate the effects on K absorption and on plant growth of two possible causative factors; first, the decreased or increased concentration of soluble K that may result from the presence of other cations, and secondly, the effect of the various soluble cations on the ability of the plant to absorb K from solution. Because of this difficulty, culture solutions offer various advantages over soil cultures in a study of this problem. On the other hand, many culture solution studies are open to criticism because of the high concentrations of various cations used as compared to those found in soil solutions, and because of the difficulty of controlling all important factors involved.

The interest among soil investigators in the effect of various cations on K absorption by plants has resulted for the most part from their endeavors to explain results obtained in three general lines of investigations; namely, the effect of liming of soils on K availability to plants, the K deficiency of certain high-lime soils, and the best form and optimum ratios of various fertilizer materials especially when used in large amounts and on slightly buffered soils. It is with the

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second of these problems that the authors have been most concerned, but consideration is given in this paper to the effect of other common cations as well as of Ca on K absorption by plants.

#### EFFECT OF CALCIUM AND MAGNESIUM ON POTASSIUM ABSORPTION BY PLANTS

##### *Liming of acid soils*

Nearly 25 years ago Ehrenberg (17) attributed the poor growth of buckwheat on heavily limed soils to the decreased absorption of K by the plant. He believed that the Ca had a depressing or antagonistic effect on K absorption, and he emphasized the importance of a proper Ca-K balance in plant nutrition. This relationship between Ca and K has since been referred to as "Ehrenberg's potash-lime law." Loehwing (35), working with cereal crops, and Lagatu and Maume (32), with grapes, found that applications of lime reduced crop yields as well as K content. Other workers who found that liming of soils decreased the K content of the crops include Brown and McIntire (8), Lipman, Blair, and Prince (34), Salter and Ames (45), and Swanback (51). In these cases, however, crop yields were increased by liming.

The K percentage in plants is, however, not always decreased by lime applications to the soil. Naftel (41) limed soils to different degrees of Ca saturation and found only very slight decreases in the K content of sorghum; Gile (18) and Ratter (44) also found that the exchangeable Ca of soils had little or no influence on the K content of the crops. Van Itallie (29) compared the effects of adding comparable amounts of Ca, Mg, Na, and K carbonates to an acid sandy soil on the absorption of these cations by Italian rye grass, and found that Ca had little effect on the absorption of K, whereas Mg had a marked depressing effect. Cooper (14), on the other hand, found that carpet grass contained a higher content of potassium on the limed than on the unlimed soils studied. That some of these contradictory results are explained by the kind of plant used in the experiment is indicated by some recent data of Bender and Eisenmenger (6). These investigators found that liming an acid soil with  $\text{Ca}(\text{OH})_2$  from about pH 4.4 to 7.3 caused a marked reduction in the potassium content of wheat and oats; a slight decrease in that of barley, sweet clover, and cowpeas; and an increase in that of peanuts, tomatoes, Kentucky bluegrass, timothy, and redtop. Liming increased the calcium content of all plants, however, in several cases from threefold to fourfold.

The variable effect on the potassium content of crops is undoubtedly influenced also by the fact that liming may either decrease or increase the water-soluble potassium content of soils. It is obvious, therefore, that unless the effect of lime on the soluble potassium content of soils is known, it is impossible to determine from such experiments whether the decreased absorption of potassium by plants is due to a lower amount in solution or to an antagonistic effect of the increased calcium concentration in accordance with Ehrenberg's law.

##### *Studies on high-lime soils*

The depressing effect of Ca and Mg on K absorption by corn has been advanced as a possible explanation for the marked deficiency symptoms and the

low K content of this crop when grown on the high-lime soils of northcentral Iowa. Allaway and Pierre (1) and Stanford *et al.* (49) have found that although many of these soils contain 150 to 200 pounds of exchangeable K per acre (2,000,000 pounds of soil), the corn shows marked K-deficiency symptoms and the yield may be more than doubled by application of potash fertilizers. An analysis of the corn on these soils as compared with that on adjoining normal soils on which good growth is obtained shows that the former has a much higher Ca and Mg content and a much lower K content (49). Figure 1 shows that the Ca + Mg:K ratios were less than 3.5 for the plants grown on the normal soils

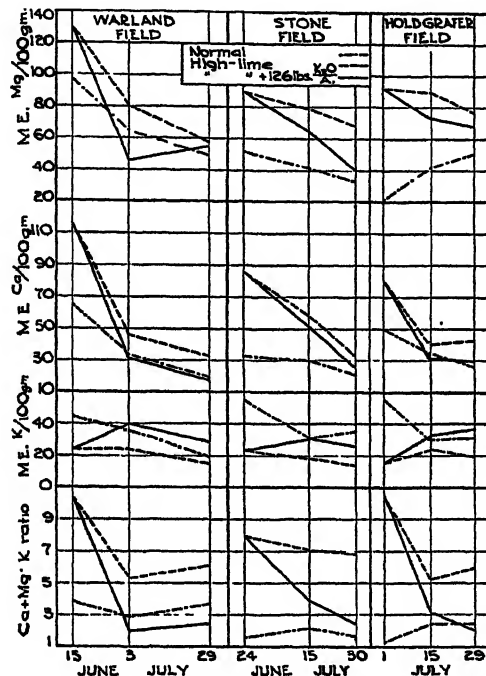


FIG. 1. COMPOSITION AND RATIO OF CALCIUM PLUS MAGNESIUM TO POTASSIUM OF CORN PLANTS FROM NORMAL, HIGH-LIME, AND POTASSIUM-FERTILIZED PLATS AT THREE DATES DURING THE GROWING SEASON

The potassium fertilizer (KCl) was applied to each field on the first sampling date

and between about 5.5 and 11.0 for those from the high-lime soils. Potassium fertilizer applied as a side-dressing resulted in a marked increase in the K content of the plant and a lowering of the Ca + Mg:K ratio.

To discover whether the low K content and poor growth of corn on high-lime soils was due to a depressing effect of Ca and Mg on K absorption, Kelly<sup>2</sup> determined the concentration of these cations in the displaced solution of high-lime and adjacent normal soils of the Webster series. The soils were brought to the

<sup>2</sup> Kelly, J. B. Composition of the displaced soil solution and exchangeable potassium content of high-lime soils in relation to potassium deficiency in corn. Master's thesis, Iowa State College, Ames, 1941. [Unpublished.]

laboratory and incubated at approximately field moisture content for 10 weeks before displacement. The data in table 1 show that the soil solutions were very high in Ca and Mg and very low in K. In two of the fields the normal soils were considerably higher in soluble K than the high-lime soils, and the lower yields and high Ca + Mg:K ratios of the crops grown on the latter could be explained by the higher K concentration in the soil solution. This explanation does not hold, however, for the data from the high-lime soil of field 3, since the K concentration in the soil solution of the two soils was of the same order. The much higher concentration of soluble Ca in the high-lime soil, however, may

TABLE 1

*Relation of Ca + Mg:K ratio of soil solution to the yield and Ca + Mg:K ratio of corn grown on high-lime and adjacent normal soils\**

DETERMINATION	FIELD 3		FIELD 4		FIELD 5	
	Normal	High-lime	Normal	High-lime	Normal	High-lime
Yield per acre.....bu.	62.8	22.4	71.3	16.9	55.8	28.8
Soil:						
CaCO <sub>3</sub> equivalence.....per cent	11.3	36.3	2.3	31.5	1.1	10.8
Exchangeable K per acre.....lbs.	270	116	405	116	187	145
Soil solution composition:						
K.....p.p.m.	2.20	1.01	12.45	0.85	0.61	0.62
Ca.....p.p.m.	350	385	250	218	207	322
Mg.....p.p.m.	70	76	56	57	46	45
Ca + Mg:K ratio†.....	413	987	54	718	904	1243
Plant composition:						
K.....m.e./100 gm.	54.7	26.5	107.1	23.6	51.1	24.1
Ca.....m.e./100 gm.	42.2	51.9	32.7	55.4	39.7	89.6
Mg.....m.e./100 gm.	75.2	116.0	39.1	101.2	79.0	95.0
Ca + Mg:K ratio†.....	2.17	6.43	0.69	6.67	2.33	7.70

\* Kelly, J. B. Unpublished data, Iowa Agr. Exp. Sta., 1941.

† Calculated on a chemical equivalent basis.

have depressed the absorption of K by the plant and resulted in a high Ca + Mg:K ratio and in low crop yield.

Although these data are far from conclusive and other factors undoubtedly are involved, it seems possible that the low absorption of K and the extremely poor crop growth on these high-lime soils is a result of the depressing effect of the high concentration of Ca on the absorption of K by the plants as well as on the amount of exchangeable K that comes into solution.

#### *Solution or sand culture investigations*

In considering the effect of various cations on the absorption of potassium it should be remembered that the K concentration in the solution of field soils is usually below 10 p.p.m., that of magnesium about 50, and that of calcium over

100. Furthermore, it has been established that a constant concentration of 2 to 5 p.p.m. of K is sufficient for optimum growth of crops in culture solutions (4, 24, 42). In many culture solution studies on nutrient balance and "ion antagonism" much higher concentrations of K have been used than are ordinarily found in the soil solution.

A review of many investigations on the effect of various cations on the growth and absorption of potassium by different plants in solution and sand cultures (2, 3, 11, 12, 15, 37, 48, 53) indicates that Ca may increase K absorption when the K concentration is high and the ratio of Ca to K relatively low, or when the concentration of Na and possibly other cations in the solutions are relatively high as compared to K; and that Ca reduces K absorption, particularly where it is added to the solution or soil in high concentrations.

#### INFLUENCE OF OTHER CATIONS ON POTASSIUM ABSORPTION

##### *Sodium*

Although Na is not essential for plant growth, it is a common constituent of plants and thus influences the cation-interrelationships in the plant. The capacity to absorb Na varies greatly among different plants (13, 28, 40). Because of this variation, it is evident that the extent of the interaction of Na and K in a given plant depends upon the specific nature of the plant as regards Na absorption. In much of the work with Na, as with Ca and Mg, it is necessary to differentiate between interactions taking place in the soil and those taking place between the plant and the soil solution. Depending upon conditions, two different interactions may occur in the soil. In the case where neutral Na salts are applied, the Na has a tendency to increase the availability of soil K to plants by increasing the K concentration of the soil solution through cation exchange. In the other case, where the soil contains appreciable quantities of exchangeable Na, this cation decreases the availability of K to plants, as shown by the work of Ratner (44). Unfortunately, in many investigations involving Na, it is impossible to separate the soil interactions from the plant interactions. Such is the case in the experiment of Van Itallie (29), who found that when the percentage Na saturation of a soil was raised from 1 to 26, the K content of Italian rye grass grown on the soil was reduced from 133.5 to 78.5 m.e. per 100 gm., while the Na content was increased from 11.5 to 97.0 m.e.

Many investigations have been carried on to determine the role of Na in plant nutrition, especially the extent to which Na can serve as a substitute for K in the fertilization of crops. The recent publication of a number of papers on this subject indicates a renewed interest in the problem. In the United States, studies with Na salts were begun at the Rhode Island Agricultural Experimental Station by Wheeler and Adams (54) in 1894 and continued by Hartwell *et al.* (21, 22, 23). Field experiments, designed to study the effects on plant growth of adding K and Na in different relative amounts, both as the chloride and as the carbonate, demonstrated that when a deficient amount of K was supplemented by a liberal amount of Na, a considerable increase in yield resulted with certain crops and that the increased yield was accompanied, in nearly all cases,



by an increase in the percentage of Na in the crop and a decrease in the percentage of K. The relative depression of K, however, which resulted when extra Na was added, was not so great in most cases as the relative increase in yield, and therefore more K was actually removed from the soil by the crop, a point which seems to indicate that at least a part of the beneficial effect of the Na was due to its ability to increase the availability of the soil K to the plant. Proof that Na had an additional beneficial effect was obtained by the use of solution cultures in which the available K could be limited to a definite amount. Using wheat, millet, oats, barley, and rye seedlings as experimental plants, Hartwell, Wheeler, and Pember (21, 22) obtained no increases in growth by the addition of Na when an optimum amount of K was present, but they found, as did Breazeale (7), that larger amounts of K were left in the nutrient solution when K was supplemented by Na, showing that Na depressed the absorption of K.

In a more recent investigation, conducted under field conditions on a muck soil by Harmer and Benne (20), applications of NaCl resulted in marked increases in Na content and slight to moderate decreases in percentage K with certain members of the beet, parsley, and mustard families. A striking example of the extent to which Na may depress K absorption by the plant is the work of Lehr (33), who grew beets at five K levels with  $\text{NaNO}_3$  and  $\text{Ca}(\text{NO}_3)_2$  as sources of N. In the foliage, the percentage decrease in K content obtained by the use of  $\text{NaNO}_3$  in place of  $\text{Ca}(\text{NO}_3)_2$  varied from 29 to 58, being highest with the high K level. In the roots the differences were not so striking, but they showed the same general trends.

### *Ammonium*

It is generally recognized that the  $\text{NH}_4$  ion is absorbed directly by many plants, and that the rate of its absorption depends upon the pH of the culture solution, a relatively high pH being most favorable. With the recent increases in the use of ammonia in fertilizers, a number of studies have been made of the relative effects of nitrates and  $\text{NH}_4$  salts on the composition and growth of various plants (16, 26, 43). One of the more detailed studies is that of Pirschle (43), who grew a variety of agriculturally important plants in flowing culture solutions maintained at various pH values. With all plants, except rice, considerably less K was adsorbed when  $\text{NH}_4$  salts were used as a source of N, and this was especially true at the higher pH values, where the  $\text{NH}_4$  plants frequently contained only half as much K as the  $\text{NO}_3$  plants. In general, better growth was obtained with  $\text{NO}_3$  than with  $\text{NH}_4$ , although maximum growth was often obtained with  $\text{NH}_4$  at pH 6 and 7.

Evidence that the effect of  $\text{NH}_4$  on K absorption varies with the level of K in the nutrient solution is found in the work of Holley, Pickett, and Dulin (26), who obtained decreases in K absorption by cotton when the nutrient solution contained 156 p.p.m. of K, and increases when it contained 19.5 p.p.m., the nitrates and  $\text{NH}_4$  salts being applied in a concentration chemically equivalent to the K in each nutrient solution. In this study,  $\text{NH}_4$  decreased the Ca and Mg absorption much more than the K absorption. This finding differed from that of

Dikussar (16), who noted that  $\text{NH}_4$  had a more pronounced depressive effect upon the absorption of K.

The effects of  $\text{NH}_4$  in reducing the absorption of K and other cations from soil have not been studied in as much detail as in culture solutions, probably because of the fact that under soil conditions it is more difficult to prevent nitrification. In table 2 are given data showing the effect of  $\text{NH}_4$  applied as  $(\text{NH}_4)_2\text{SO}_4$  on the absorption of K, Ca, and Mg by corn from two acid soils. As a result of concentrating the fertilizer in a soil zone constituting 10 per cent of the soil in the pots, virtually no nitrification took place. The plant composition data show that the application of  $(\text{NH}_4)_2\text{SO}_4$  under these conditions has very materially depressed K absorption but has had little effect on Ca and Mg absorption.

TABLE 2

*Effect of addition of  $\text{NH}_4$  and Ca to two acid soils in different nitrogen fertilizers on the absorption of K, Ca, and Mg by corn\**

TREATMENT†	CORN ON WHEELING FINE SANDY LOAM, pH 5.0					CORN ON DE KALB SILTY CLAY LOAM, pH 4.8				
	K	Ca	Mg	Ca+Mg K	Yield per pot	K	Ca	Mg	Ca+Mg K	Yield per pot
	m.e./100 gm.	m.e./100 gm.	m.e./100 gm.		gm.	m.e./100 gm.	m.e./100 gm.	m.e./100 gm.		gm.
None.....	33.1	16.3	9.2	0.77	38.5	43.9	19.5	7.6	0.62	20.1
150 lbs. of N as Ca $(\text{NO}_3)_2$ per acre...	19.7	25.1	9.5	1.76	68.5	23.8	25.5	8.1	1.41	52.9
150 lbs. of N as $(\text{NH}_4)_2\text{SO}_4$ per acre..	18.0	19.2	7.5	1.48	68.3	23.2	15.9	7.6	1.01	58.3

\* Pierre, W. H. Unpublished data, W. Va. Agr. Exp. Sta., 1937.

† In addition, all pots received 200 pounds of  $\text{CaH}_4(\text{PO}_4)_2$  and 100 pounds of KCl per acre.

### Iron

Hoffer and Trost (25) found that the Fe content of corn nodes is higher when the plant is deficient in K. These results were confirmed by Scharrer and Schropp (46, 47), who considered the phenomenon to be one of antagonism. Some doubt as to the correctness of this interpretation is found in the data of Weiss,<sup>3</sup> who showed that in K-deficient soybean plants, the pH of the sap and the total Fe content were higher, whereas the soluble Fe content was lower. Loehwing (36) also found that high pH values of the sap are associated with K deficiency. In view of these results, it seems probable that the high Fe content of K-deficient plants is due to the higher pH values of the sap, a condition which brings about the precipitation and accumulation of Fe in abnormal amounts.

### Manganese

Swanback (50) has studied K absorption by tobacco in terms of percentages of quantities supplied in nutrient solutions having various K and Ca levels, in the presence and absence of Mn. The efficiency of K utilization was greater in

<sup>3</sup> Weiss, M. G. Inheritance and physiology of efficiency in iron utilization in soybeans. Doctoral thesis, Iowa State College, Ames, 1941. [Unpublished.]

the absence of Mn at low Ca and at high K levels. The reverse was true at high Ca and low K levels. The greatest relative utilization of K occurred at low K levels in the presence of Mn. The data on this subject are too scanty to justify any conclusion; furthermore, the effect of Mn on K absorption is probably of little practical importance in view of the very small quantities of Mn ordinarily found in the soil solution.

#### FACTORS AFFECTING THE INFLUENCE OF VARIOUS CATIONS ON POTASSIUM ABSORPTION

Although investigations on "ion substitution" or "replacement" are still much too fragmentary for a satisfactory understanding of this phenomenon, it appears that at least six factors may influence the effect of other cations on potassium absorption by plants. These are:

1. Level of K.
2. Concentration of cation in relation to K concentration.
3. Kind of cation.
4. Presence of other cations.
5. Kind of plant.
6. pH of solution.

The importance of some of these factors has already been referred to and they will be reviewed here only briefly.

##### *Level of potassium*

The level of K in solution will determine to a large extent whether or not the depressing effect that may be exerted by other cations will reduce the amount of K absorbed below the plant needs and thus cause decreased growth. It is not possible to determine definitely from the data available, however, whether or not with a given ratio of cations, the depression in absorption of K occurs more readily at high than at low K levels. The investigations of Holley, Pickett, and Dulin with cotton (26) show that with a constant ratio between K and  $\text{NH}_4$  the depression in absorption of K by  $\text{NH}_4$  occurred only at high levels of the ions. Although this is apparently the only direct evidence on this question, it seems quite probable that with high concentration of cations, "ion competition" is more pronounced than at low concentrations, the ratio of cations remaining constant.

##### *Concentration of cation in relation to K concentration*

In general it has been found that the higher the concentration of a particular cation in relation to the concentration of K, the greater is the depression in the absorption of the latter by plants (29). In fact, it has been shown by several investigators (2, 37, 53) that when the concentration of Ca relative to that of K is low, the Ca actually favors K absorption by the plants, and it is only when the Ca is materially increased that K absorption is depressed. This is in general agreement with results based on deficiency symptoms and growth responses (15, 19). Thus Davidson and Blake (15) found that where 10 p.p.m. of K was present in

solution the K-deficiency symptoms in peach were obtained only with high Ca levels (410 p.p.m.), whereas with only 2 p.p.m. K, the peach leaves showed deficiency symptoms with the medium Ca level (180 p.p.m.). These results are to be expected, for the higher the concentration of a cation in solution in contact with the roots, the greater will be its ability to "compete" with potassium for entrance into the root.

### *Kind of cation*

No doubt one of the most important factors affecting K absorption by plants is the kind of complementary cation. Lundegårdh (38) concluded from his investigations that the substitution of cations is strongest between the outermost ions of the following series: Mn, Ca, Mg, K, and Na. In his rather comprehensive work with Italian rye grass, Van Itallie found that the replacing or competing abilities of the various cations are in the order:  $K > Na > Mg > Ca$ . That Ca has the least competitive ability and K the greatest of the four cations listed is evidenced too by the work of other investigators (3, 11, 44).

The position of Na in the cation competition series, however, seems to vary considerably, possibly because of the wide differences in the capacities of various plants to absorb Na from solution. Carolus' work with potatoes, a low-sodium plant (28), shows, for example, that Na depressed K absorption less than did Mg. It is evident, therefore, that monovalent cations are not necessarily more effective in cation replacement than divalent cations. This is substantiated by Hurd-Karrer (27) and by the recent work of Collander (13), who found that cation replacement was most marked between the closely related cations Ca and Sr, and K and Rb than between the divalent and monovalent cations.

It is evident, therefore, that the nature of the cation has a marked effect on the concentration required to depress the absorption of K by plants. In general, Ca has a lower activity in this respect than Mg and Na, but the effect of Na, like that of  $NH_4$ , seems to be more variable.

### *Presence of other cations*

As has previously been indicated, there is evidence that the effect of one cation on the absorption of another will be affected by other cations in solution. The data with potatoes and beans reported by Carolus (11, 12) show definitely that in the presence of large amounts of sodium, Ca enhanced rather than depressed the absorption of K. Likewise, in the presence of large amounts of Ca or Mg, sodium had a beneficial effect rather than a depressing effect on K absorption by potatoes, although not by beans. That the kind and amount of anions in solution may also influence the importance of cation ratios in the nutrient solution is shown by the investigation of Beckenbach *et al.* (5). With high  $NO_3$  levels, K appeared to be necessary in greater concentration than Ca, indicating that Ca under such conditions is more readily absorbed by corn than is K.

### *Kind of plant*

Probably the most important single factor that influences the effect of one cation on the absorption of another is the plant species. Many of the seemingly

conflicting data that have been noted could undoubtedly be explained if more data were available concerning the nutrition of different plants. The recent work of Bender and Eisenmenger (6), in which they found that the liming of an acid soil had a marked effect in reducing the K content of certain crop plants, had no effect on others, and actually resulted in an increase in the K content of still others, emphasizes this point.

Since it is well known that plants vary widely in the ratio of the different cations they absorb from the same nutrient solution or soil, it might seem that the more readily a plant absorbed a given cation, the greater would be the depressing effect of that cation on the absorption of another, other factors remaining the same. Actually, Lundegårdh (38) explained the detrimental effect of a high K concentration on the Ca absorption by sugar beets on the basis that this crop absorbs extraordinarily large amounts of K. Although some evidence supports such a hypothesis, other evidence does not. For example, the potato is a low-sodium plant, according to Van Itallie (28). Yet the data of Carolus (11) show that Na greatly inhibits K absorption by potatoes. Moreover, it is well known that on high-lime soils containing a high Ca to K ratio in the soil solution, corn exhibits extreme symptoms of K deficiency, whereas sweet clover, a crop much higher in Ca, grows normally. It would seem, therefore, that the effect of a high concentration of a given cation on the absorption of K from solution cannot be explained solely by the ease with which the former is normally absorbed and consequently by its greater competition with K absorption, but that its effect may also be exerted in some other way, possibly on the permeability of the root cells.

#### *pH of solution*

There is considerable evidence to show that in culture solutions Ca and  $\text{NH}_4$  are more readily absorbed at pH values above neutrality than at lower pH values, whereas K is either little affected or acts exactly the reverse. Thus, Arnon *et al.*<sup>4</sup> in carefully controlled experiments with lettuce and Bermuda grass found maximum absorption of Ca at the most alkaline reaction, pH 9.0 (range 3–9), whereas over the pH range 4–9 no profound effect on K or Mg absorption was noted. Similar results regarding absorption of Ca at various pH values were obtained by Bryan (9, 10) with alfalfa, alsike, and red clover. With oats and wheat, however, absorption of Ca was about the same at all pH values, indicating that various plants behave differently in this respect. Jacques (30), working with *Nitella*, found that pH had no influence on the rate of entrance of K, if the K concentration was above 3.9 p.p.m. When the concentration was reduced to 0.6 p.p.m., however, he found that the rate of K absorption decreased as the pH increased from 6.0 to 8.0. In the case of  $\text{NH}_4$ , the data of Pirschle (43) clearly show that depression of K absorption is greatest at high pH values.

In view of these results, it might be expected that Ca and  $\text{NH}_4$  would tend to depress K absorption more at high than at low pH values. Some evidence for

<sup>4</sup> Arnon, D. I., Fratzke, W. E., and Johnson, C. M. Hydrogen ion concentration in relation to absorption of inorganic nutrients by higher plants, 1941. [Unpublished.]

the greater depressing effect of Ca on K absorption at high than at low pH values is found in the work of Barbier (3). Substantiation of such data, if possible, would tend to explain the potassium deficiency of plants grown on high-lime soils having high ratios of Ca to K in the soil solution.

#### GENERAL CONCLUSIONS

It is evident from this discussion that the problem of "cation competition" and "replacement" in plant nutrition is complicated and that many more careful studies must be made before it is adequately understood. In this review the writers have been primarily concerned with the relation between the relative concentration of cations in solution and their absorption by plants. It is recognized, of course, that this is only one phase of the problem of the availability of K and other nutrient cations of the soil, and moreover, that more consideration must be given in this regard to the contact exchange theory of plant feeding proposed by Jenny and Overstreet (31).

Some of the more important general conclusions that may be drawn concerning the effect of other cations on K absorption from solution are as follows:

Potassium absorption by plants is usually decreased by the presence of high concentration of other cations in solution. Under certain conditions, however, it may be increased.

The decreased absorption of potassium may have a detrimental effect, a beneficial effect, or no effect on yield, depending on the amounts absorbed in relation to the needs of the plant.

Since K has a higher "competitive ability" than other common cations, the decrease in K from high concentrations of other cations is not so pronounced as is the effect of K on the absorption of Ca or Mg.

The effect of various cations on the absorption of K by plants depends on a number of different factors, many of which are additive. Among these factors, the plant species and the ratio of other cations to K are probably dominant.

The high ratio of Ca and Mg to K in the soil solution of the high-lime soils of Iowa may be an important contributing factor to the low availability of the potassium in these soils to corn and other crops. The high nitrate content and high pH value of these soils probably increase the depressive effect of Ca and Mg on K absorption.

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# THE EFFECT OF LIME AND MAGNESIA ON THE SOIL POTASSIUM AND ON THE ABSORPTION OF POTASSIUM BY PLANTS

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The influence of lime and magnesia on the behavior of soil potassium and on the absorption of potassium by plants is a highly controversial subject, as shown by several very recent publications. As little agreement seems to exist among plant physiologists as among soil chemists. This apparent confusion, in the soil literature at least, has arisen largely because of failure by many investigators to evaluate critically the experimental conditions under which the results were obtained and to differentiate between the physiological ion interactions, on one hand, and the soil Ca-K or Mg-K interactions on the other.

This paper is confined principally to a discussion of the effect of lime and magnesia on the soil potassium and to a critical examination of some of the apparently conflicting results obtained in both soil and plant studies concerning the intricate Ca-K and Mg-K relationships. With due recognition of the significant recent investigations on the contact exchange absorption mechanism of plants (24), the authors assume, for purposes of the present discussion, that the plants absorb the greater part of their nutrient cations from soil solution.

## REVIEW OF THE LITERATURE

It was once thought, and is still held by some investigators, that lime tends to liberate the soil potassium. Subsequent investigations, particularly the extensive lysimeter studies of MacIntire and his associates (31), have shown conclusively that lime exerts a repressive effect on the solubility of soil potassium. Guthrie and Cohen (21) found that only in sandy soils did liming have any effect in increasing the amount of water-soluble potassium. Lipman and Gericke (26) also questioned the liberation of soil potassium by lime. Gaither (18) concluded that little, if any, potassium is made available by liming. Wheeler (47) asserted that "liming was of no great value on the Kingston soil as a liberator of potassium." Fraps (16) found no appreciable liberation of potassium by lime as measured by solubility in dilute acid or the amounts removed by crops. Lyon and Bizzell (29) reported that lime did not increase the quantity of potassium in the drainage water or in the crop. Wilson (48) showed that heavy applications of lime to different soils had no consistent effect on the exchangeable potassium. Ames and Simon (3) found a larger amount of water-soluble potassium in the unlimed than in the limed soil due to greater adsorption of potassium by the limed soil. Brown and MacIntire (10) also reported that water extractions of soils from the Pennsylvania plots showed more potassium in solution in the unlimed soil than in the limed soil. Shedd (42) found that  $\text{CaCO}_3$  decreased the solubility of soil potassium in water and reduced the amount extracted with ammonium nitrate solution. Schollenberger and Dreibelbis (39), in their studies on the fertility plots at Wooster, Ohio, found that the exchangeable potassium content of the limed soil was only slightly lower than that of the unlimed soil. Naftel (32) also found that the exchangeable potassium was reduced with each increment of  $\text{CaCO}_3$ , but the addition of  $\text{CaCO}_3$  and  $\text{MgCO}_3$  in equivalent amounts increased considerably the amount of exchangeable potassium. McGeorge (30) reported that the exchangeable potassium is readily replaced from calcareous soils by ammonium salts but not by calcium salts. Allaway and Pierre (2) showed that unproductive high-lime soils of Iowa contained less exchangeable potassium, fixed

more potassium into nonexchangeable form, and showed a less rapid liberation of the non-exchangeable potassium than the adjacent normal soils. Bradley (9) found that lime gave increases in soluble potassium. Bradfield (7) pointed out that failure to consider the soil acidity has led to many disputes concerning the question of liberation of soil potassium by lime and showed that, unlike  $\text{CaSO}_4$ ,  $\text{CaCO}_3$  cannot appreciably liberate soil bases until the acidity of the soil is neutralized. Jenny and Shade (23) pointed out that "without a single exception, all laboratory experiments performed by the authors show that  $\text{CaCO}_3$  liberates adsorbed potassium from soil colloids" and suggested that the depressive effect of lime on the availability of potassium may be due to fixation of potassium by soil micro-organisms. The possibility of lime-induced microbiological fixation of potassium was also indicated by Dean (12).

The literature is also conflicting in views concerning the effect of lime and magnesia on the absorption of potassium by plants. In extensive discussion of the subject, Ehrenberg (13) points out that, as lime additions are increased, the assimilation of potassium by the plant decreases, often resulting in an injury to the plant on soils with a limited supply of potassium. This suppressive effect of lime on the uptake of potassium by plants has been observed by many investigators, among whom may be mentioned Loehwing (28), Nemec and Gracanin (33), Bledsoe (5), Plummer (37), Fonder (15), Brown and McIntire (10), Salter and Ames (38), Lipman, Blair, and Prince (27), Swanback and LeCompte (44), and Stanford, Kelly, and Pierre (43).

According to other investigations, lime either has no effect or actually favors the assimilation of potassium by plants. Gunther (20) found no change in the absorption of potassium by plants upon addition of increasing amounts of lime to an acid soil. Jenny and Ayres (25), in their studies of the influence of degree of saturation on the nutrient intake by barley roots, found that exchangeable calcium had little effect on the uptake of potassium. Van Itallie (22) also found that increasing the amount of exchangeable calcium in the soil showed but little influence on absorption of potassium by Italian rye grass. Wrenshall and Marcello (51) concluded, from results of field experiments, that lime had little or no effect on the utilization of potassium by plants. Gericke (19), however, found by Neubauer's method that the amount of potassium absorbed by the plants was actually increased by large applications of lime. Very recently, Albrecht and Schroeder (1, 40) reported that the percentage of potassium, as well as the total amount absorbed by spinach and potato tops from colloidal clay cultures increased with increasing supply of exchangeable calcium. They (40) wrote that "rather than 'antagonistic' effect of the calcium on the potassium, there is apparently a 'synergistic' effect, in that the calcium is associated with movement of potassium into the tops."

From the literature cited, it is obvious that the calcium-potassium relationship both in soils and in plants is not only obscure but confusing.

#### DISCUSSION

##### *Effect of lime and magnesia on the soil potassium*

Although the amount of exchangeable potassium in the soil at any one time is rather small and more or less constant, it is generally believed that this form, being in equilibrium with that in soil solution, represents the immediate source of readily available potassium for plants. There are two ways, then, in which lime may decrease the availability of soil potassium: first, by inducing the conversion of exchangeable potassium into nonexchangeable forms, and second, by enhancing the power of the soil colloids to adsorb the potassium from soil solution, thus displacing to the left either one or both of the soil potassium equilibria indicated below:



It should be pointed out here that Wood and DeTurk (49) do not consider potash fixation in nonexchangeable forms as being detrimental to crop utilization, since the fixed potassium is in equilibrium with the exchangeable form.

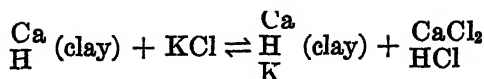
*Effect of lime on equilibrium I.* There is some evidence that lime promotes fixation of potassium into nonexchangeable forms. Sears (41), working with an infertile calcareous soil, found that this soil was capable of fixing potassium in nonreplaceable form. That lime additions may induce potassium fixation in some soils at least, was shown by Volk (46); however, the increases in fixation due to lime were small in proportion to the potassium-fixing capacity of the soils. In their investigations of potassium-deficient calcareous soils of Iowa, Allaway and Pierre (2) showed that the calcareous soils fixed much larger amounts of potassium into nonexchangeable forms than did the acid upland soils. Blume and Purvis (6) also found that liming increased the fixation of potassium into nonexchangeable form. Peech and Bradfield (35) did not detect potassium fixation in Miami colloidal clay regardless of the degree of calcium saturation. Worsham and Sturgis (50) found little difference in potassium fixation between calcium- and the corresponding hydrogen-saturated soils. Wrenshall and Marcello (51) found that lime had no effect on potassium fixation under field conditions. In their laboratory studies, however, they found that, without addition of potassium, lime applied at the rate equivalent to 25 tons per acre had virtually no effect on potassium fixation, but when 1,000 pounds per acre of  $K_2O$  was added as the chloride, lime increased slightly the fixation of potassium into non-exchangeable form.

Although it has been shown that certain calcareous soils possess a high capacity to fix potassium into nonexchangeable form and that, in some soils, lime increases potassium fixation, it is questionable whether moderate applications of lime, even over a long period of time, under practical field conditions, promote significant conversion of the native or added potassium into nonexchangeable forms, and if so, whether this would be reflected in the crop utilization of potassium.

Little information is available on the influence of lime on the rate of conversion of potassium from nonexchangeable to exchangeable form, but it seems reasonable to suppose that the rate of conversion would increase with increasing acidity of the soil, as in the case of the primary potassium-bearing minerals like biotite and orthoclase reported by Peech and Bradfield (35). The work of Fine, Bailey, and Truog (14) also indicates that lime tends to inhibit the release of fixed potassium upon freezing and thawing.

*Effect of lime and magnesia on equilibrium II.* The equilibrium between the exchangeable potassium and that in soil solution (equilibrium II), as affected by lime and magnesia, has been studied perhaps in greater detail than equilibrium I. Peech and Bradfield (35) investigated the adsorption of potassium from KCl by Miami colloidal clay as a function of the degree of saturation of the clay with calcium and magnesium, and in the presence of excess  $CaCO_3$  and  $MgCO_3$  brought in equilibrium with the partial  $CO_2$  pressure of the air. Portions of their data are presented graphically in figures 1 and 2.

In the reaction,



potassium from KCl replaces Ca more readily than H on the clay, because of the relative position of Ca and H in the lyotropic series. The extent to which this reaction will proceed to the right will depend largely, therefore, on the initial degree of Ca-saturation of the clay. It should be obvious from this reaction that *an increase in the degree of calcium saturation will favor the adsorption of potassium from its neutral salts, whereas an increase in Ca-ion concentration will effect the liberation of the adsorbed potassium.* As shown in figure 1, the adsorption of

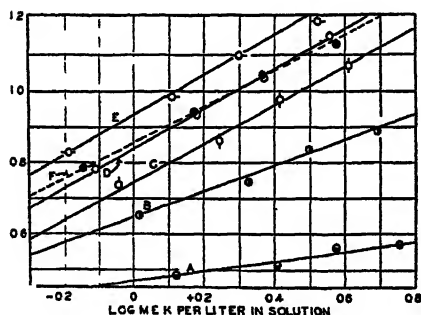


FIG. 1

FIG. 1. ADSORPTION OF K FROM KCl BY CLAYS SATURATED WITH VARYING AMOUNTS OF Ca

A, H-clay; B, 25 per cent Ca-saturated clay; C, 50 per cent Ca-saturated clay; D, 75 per cent Ca-saturated clay; E, 100 per cent Ca-saturated clay; F, Ca-clay in the presence of an excess of  $\text{CaCO}_3$  brought in equilibrium with the partial  $\text{CO}_2$  pressure of the air.

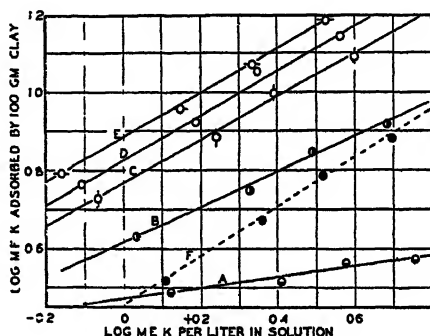


FIG. 2

FIG. 2. ADSORPTION OF K FROM KCl BY CLAYS SATURATED WITH VARYING AMOUNTS OF Mg

A, H-clay; B, 25 per cent Mg-saturated clay; C, 50 per cent Mg-saturated clay; D, 75 per cent Mg-saturated clay; E, 100 per cent Mg-saturated clay; F, Mg-clay in the presence of an excess of  $\text{MgCO}_3$  brought in equilibrium with the partial  $\text{CO}_2$  pressure of the air.

potassium from solution increased rapidly with increasing degree of calcium saturation of the clay. The potassium adsorption isotherm, for clays to which an excess of  $\text{CaCO}_3$  had been added and brought in equilibrium with the  $\text{CO}_2$  of the air, dropped immediately below that for clays which were just 100 per cent saturated with calcium. This was due, of course, to the rapid increase of Ca ions in solution, resulting from addition of an excess of  $\text{CaCO}_3$ . Bradfield and Allison (8) have shown that a true equilibrium is reached under these conditions. The clay will have adsorbed a maximum amount of calcium, and a definite concentration of Ca ions will exist in solution, depending upon the partial  $\text{CO}_2$  pressure of the air. It is interesting to note that, even in the presence of an excess of  $\text{CaCO}_3$ , the adsorption of potassium by Ca-clay was considerably greater than that by H-clay. As might be expected, the influence of magnesium

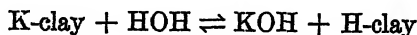
on the clay upon the adsorption of potassium from KCl, as shown in figure 2, was similar to that of calcium except that the adsorption of potassium was reduced considerably more in the presence of an excess of  $\text{MgCO}_3$  than in the presence of an excess of  $\text{CaCO}_3$ , because of the greater solubility of  $\text{MgCO}_3$  in equilibrium with the  $\text{CO}_2$  of the air. In fact, the adsorption of potassium in the presence of an excess of  $\text{MgCO}_3$  was reduced below that of clay 25 per cent saturated with magnesium. The final effect of the addition of lime and magnesia to a soil on the adsorption of potassium from neutral salts is thus determined by the reciprocal effects of the adsorbed calcium (or magnesium) and the Ca (or Mg) ions in solution. It is evident from figure 1 that, on acid soils, lime will *decrease* the potassium in soil solution because of the increase in the amount of adsorbed calcium and, consequently, greater adsorption of potassium from its neutral salts. When applied to soils already saturated with calcium, lime will liberate the adsorbed potassium and *increase* its concentration in soil solution. On slightly acid soils, where the influence of the small increase in the calcium saturation may just offset the liberative effect of the Ca ions brought into solution, lime will have *no effect* on the potassium concentration in soil solution. This may partly account for some of the apparently contradictory results relative to the liberative action of lime on the soil potassium obtained hitherto by different investigators. It is also evident why  $\text{CaSO}_4$  should invariably liberate the adsorbed potassium regardless of the initial degree of base saturation of the soil. When applied to an acid soil,  $\text{CaSO}_4$  cannot appreciably increase the degree of calcium saturation through hydrogen exchange; however, because of the comparatively high solubility of this salt (26 m.e. per liter), the Ca ions in solution will invariably liberate the adsorbed potassium. This is in agreement with the results reported by other investigators. The foregoing generalizations concerning the effects of lime and magnesia, based on the studies of adsorption by clays, of potassium added as KCl, should be equally valid when applied to soils to which no neutral potassium salts necessarily had been added, provided, of course, that any soluble neutral salt (chloride, sulfate) is present. These findings were confirmed recently by Ayres (4).

In light of the experiments just discussed, it can be readily seen why lime and magnesia should, under certain conditions, exert a suppressive effect on the solubility of soil potassium as measured by lysimeters and water extractions. The comments of Sears (41) on the high adsorptive capacity of a calcareous soil to remove potassium from solution, and of Ames and Simon (4) on the greater adsorption of soluble potassium by the limed soil, as compared with the unlimed soil, are noteworthy here. Shedd (42) also observed that "lime increases the capacity of the soil to adsorb soluble K."

Inasmuch as some significance has been attached to the Ca/K ratio in soil solution in connection with the Ca-K interactions in plants, it may be well to point out here that additions of  $\text{CaCO}_3$  and  $\text{MgCO}_3$  may actually induce great variations in the Ca/K or Mg/K ratio of the soil solution. The increased adsorption of potassium and the corresponding diminution in potassium concentration of soil solution, with the increasing degree of calcium and magnesium

saturation shown in figures 1 and 2, were accompanied by an approximately equivalent exchange of calcium and magnesium into solution. For a given amount of potassium added, as the potassium-ion concentration in solution decreased, the Ca- or Mg-ion concentration in solution increased with the respective increase in the degree of Ca- or Mg-saturation. Because of the inverse Ca-K or Mg-K relation in soil solution, the ratio Ca/K or Mg/K of the solution was found to increase very rapidly with the increasing degree of calcium or magnesium saturation respectively. The interesting observation of Pierre (36) regarding the relation between the Ca/K ratio in soil solution and the pH of the soil is pertinent. He found that, with increasing pH of soils, the calcium concentration increased while the potassium concentration in soil solution decreased; in consequence, the Ca/K ratio increased rapidly with the increasing pH. In discussing the ecological significance of the  $\frac{K + Na}{Ca}$  ratio in soil solution, Pear-sall (34) also quoted Olsen's work showing that the ratio  $\frac{K + Na}{Ca}$  in carbonated-water extracts decreased with the increasing pH of soils.

Thus far, our discussion has been limited to the influence of  $CaCO_3$  and  $MgCO_3$  on the equilibrium between the exchangeable potassium and the potassium in soil solution (equil. II) in the presence of neutral salts. If we exclude the presence of any neutral salts (of strong acids), the potassium in soil solution is determined largely by hydrolysis, as would be the case, for example, in soils of humid regions to which no fertilizer had been recently applied. Conductometric titrations of hydrogen clay with bases show that there is no appreciable hydrolysis until the clay is nearly saturated. The presence of exchangeable hydrogen should, therefore, decrease the hydrolysis of the adsorbed potassium in accordance with the mass law:



$$K^+ = K_h \frac{(K\text{-clay})}{(H\text{-clay})}$$

where  $K_h$  is the hydrolysis constant of K-clay. In tables 1 and 2 are listed some of the unpublished results of Peech,<sup>1</sup> who studied the hydrolysis of K-clay in the presence of increasing additions of H-clay and Ca-clay, using Miami electro-dialyzed colloidal clay ( $0.1 \mu$  effective diameter). Unless otherwise indicated, the clays were ultrafiltered, hydrogen gas being used for pressure to prevent contamination with  $CO_2$ , followed by determination of potassium in solution. As shown in table 1, the addition of H-clay to a constant amount of K-clay decreased the concentration of potassium in solution but did not suppress the hydrolysis of K-clay sufficiently to give a constant value for the hydrolysis constant, which varied from  $1.9$  to  $21.3 \times 10^{-5}$ . The results given in table 2 show the influence of various increments of Ca-clay on the hydrolysis of K-clay. Assuming that the activities of the adsorbed cations are not affected by one

<sup>1</sup> Peech, M. The effect of lime and neutral calcium salts on the solubility of soil potassium. Doctoral dissertation, Ohio State University, 1933. [Unpublished]

another, it is reasonable to suppose that  $\text{Ca}(\text{OH})_2$  produced by the hydrolysis of Ca-clay should inhibit the hydrolysis of K-clay. On the contrary, an anomalous effect of Ca-clay on the hydrolysis of K-clay was actually found, in that the presence of Ca-clay increased the potassium concentration in solution. This effect of Ca-clay was more pronounced in the absence of  $\text{CO}_2$  than in the aerated series (brought to equilibrium with  $\text{CO}_2$  of the air). As might be expected, the amounts of potassium found in solution were greater in the aerated than in the nonaerated series. The addition of  $\text{CaCO}_3$  to K-clay (number 5 in the aerated series) resulted in a marked liberation of the adsorbed potassium. From simultaneous consideration of the combined effects of H-clay and Ca-clay on the

TABLE 1  
*Effect of H-clay on hydrolysis of K-clay*

K-CLAY	H-CLAY	K IN SOLUTION	$K_s \times 10^5$	pH
<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>		
0.645	0	0.0340	1.9	9.50
0.645	0.258	0.0165	7.2	7.45
0.645	0.645	0.0157	16.5	6.32
0.645	0.903	0.0146	21.3	6.20

Final volume 100 ml.

TABLE 2  
*Effect of Ca-clay on hydrolysis of K-clay*

NUMBER	K-CLAY	Ca-CLAY	IN THE ABSENCE OF $\text{CO}_2$		AERATED	
			K in soln.	pH	K in soln.	pH
	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>		<i>m.e.</i>	
1	0.645	0	0.0340	9.50	0.094	8.22
2	0.645	0.258	0.0390	9.20	0.104	8.12
3	0.645	0.645	0.0450	8.90	0.105	8.00
4	0.645	0.903	0.0525	8.90	0.100	8.20
5	0.645	0*	....	....	0.363	9.00

\* Number 5 in the aerated series received 0.15 gm.  $\text{CaCO}_3$ . Final volume in each case 100 ml.

hydrolysis of K-clay, it is obvious that, for a given degree of potassium saturation, the extent of hydrolysis of the adsorbed potassium will increase rapidly with the increasing degree of calcium saturation. This is substantiated by the experiments of Jenny and Shade (23), who reported that "as soon as  $\text{CaCO}_3$  is added large amounts of K are replaced in every case, even in the acid system where not enough  $\text{CaCO}_3$  had been introduced to neutralize all the exchangeable H ions."

It is evident that the influence of lime on the equilibrium between the adsorbed potassium and that in soil solution (equilibrium II) in the absence of neutral salts is quite different from that in the presence of neutral salts of strong acids. The matter is still more complicated because the effect of lime on soil



potassium in the presence of neutral salts may work in opposite direction to that in the absence of neutral salts, and failure to differentiate between the two cases is certain to lead to erroneous conclusions. It is no wonder that considerable confusion has arisen relative to the action of lime on the native and added potassium in the soil.

*Influence of lime and magnesia on the absorption of potassium by plants*

The repressive effect of lime on the absorption of potassium by plants as well as the inverse Ca-K relationship commonly observed in plants has been attributed by some investigators to "ion antagonism," or more properly termed "mutual ion replacement" and "ion competition" (11, 22). An excellent illustration of this inverse relation, with a high degree of correlation, between the amounts of potassium and calcium in alfalfa plants grown on different soil types of varying texture has been presented by Fonder (15), who regarded this inverse relationship as a natural physiological balance, being in turn determined by the available calcium and potassium supply in the soil. Agreement appears to be lacking, however, among plant physiologists on Ca-K interaction in plants. Collander (11), for example, found that ion antagonism or ion replacement in the plant was confined to closely allied cations (not between divalent and univalent cations) and demonstrated that the uptake of potassium was rather independent of the calcium concentration of the culture solution. In a recent article Viets (45) presented data to show that the presence of either calcium or magnesium in the nutrient solution appreciably increased the absorption of potassium by barley roots. He questions the antagonistic effect of calcium on the absorption of potassium by plants and believes that the experiments upon which the concept of ion antagonism was based, were performed with high and often toxic concentration of salts. Van Itallie (22), working with soil in which the exchangeable cations were varied widely, demonstrated that mutual cation replacement took place in the plant in nearly equivalent amounts. The replacement value was largest for potassium and decreased progressively for sodium, magnesium, and calcium in the order given. Thus, the exchangeable potassium greatly diminished the uptake of Ca by Italian rye grass, whereas increments of exchangeable calcium showed but little influence on the absorption of potassium. Magnesium, however, distinctly depressed the uptake of potassium.

On the basis of the evidence just discussed, it would appear that the uptake of potassium by plants is not affected appreciably by calcium, whereas potassium, the cation which is most readily absorbed by plants, suppresses the uptake of both calcium and magnesium. Accordingly, the inverse Ca-K relationship in plants may be regarded as being primarily controlled by the available supply of potassium and comparatively little affected by the available calcium supply in the nutrient medium. In accepting this view, it is hard to reconcile the fact that plants absorb greater quantities of potassium from sandy soils low in exchangeable potassium than from heavier soils containing larger amounts of exchangeable potassium and calcium (15, 17) without assuming that when the concentration of calcium, and particularly the Ca/K ratio, in the soil solution become very high, calcium does exert a suppressive effect on the uptake of potas-

sium by plants. It has been shown how the addition of lime to an acid soil containing neutral salts will appreciably increase the calcium concentration, simultaneously decrease the potassium concentration, and thus very markedly increase the Ca/K ratio in soil solution. Under such conditions, *the addition of lime will result in decreased absorption of potassium by the plants, the observed suppressive effect of lime being induced primarily by Ca-K interactions initiated in the soil.* Not precluding the possibility of lime-induced fixation of potassium into nonexchangeable forms in calcareous soils (2), the fact that such soils have been found to respond markedly to potassium, even when supplied with exchangeable potassium in quantities greater than is normally found in productive acid soils, would also lead us to believe that the low potassium-supplying power of these soils is due to the low concentration of potassium and the high Ca/K ratio of the soil solution. It has already been pointed out that the effects of addition of lime to a soil containing neutral salts on the potassium concentration and on the Ca/K ratio of soil solution may be variable, depending upon the initial degree of base saturation of the soil. That the effects of lime on the uptake of potassium by plants under such conditions may also be variable is attested by the conflicting results often observed on soils containing neutral salts.

Returning now to the action of lime on the soil potassium in the absence of neutral salts, it will be recalled that, in this case, the addition of lime will liberate the adsorbed potassium even when an insufficient amount is added to neutralize all of the exchangeable hydrogen. Since the calcium concentration in the soil solution will not be increased appreciably until an excess of  $\text{CaCO}_3$  is added, one would expect that moderate applications of lime to an acid soil in the absence of neutral salts should invariably increase the potassium concentration but should have comparatively little effect on the Ca/K ratio in soil solution. In such a case, *the absorption of potassium by the plants should remain unaffected or may be even increased by the addition of lime.* Unfortunately, only few experiments reported in the literature can be cited in support of this statement, because the chemical characteristics of the soil and other experimental conditions under which the results were obtained are often lacking. Van Itallie (22), working with soils in which the variations in the relative amounts of the *adsorbed* cations were effected by the addition of the hydroxides of the respective cations to an acid soil, reported that increasing amounts of exchangeable calcium had little influence on the uptake of potassium by plants. More recently, Albrecht and Schroeder (1, 40) reported that the percentage of potassium and the total amount of potassium absorbed by spinach and potato tops from colloidal clay cultures increased with increasing additions of Ca-clay to a constant amount of K-clay. It may be concluded, therefore, that when the experimental conditions are properly evaluated, the apparently conflicting results reported concerning the intricate Ca-K relationships in soils and plants are indeed in fairly good agreement.

#### SUMMARY

A critical review of the literature reveals that the apparent confusion concerning the effect of lime and magnesia on the soil potassium and on the absorption

of potassium by plants has arisen largely because of failure to evaluate properly the experimental conditions under which the results were obtained and to distinguish the Ca-K interactions in the soil from those in the plant. The addition of lime to soils containing neutral salts (of strong acids) may have no effect, may decrease, or may increase the concentration of potassium in soil solution, depending upon the initial degree of base saturation of the soil. In the absence of neutral salts, the addition of lime will invariably liberate the adsorbed potassium even when an insufficient amount is added to neutralize all of the exchangeable hydrogen. Experimental facts regarding the influence of lime on the uptake of potassium by plants can be readily interpreted in the light of these effects of lime on the soil potassium, particularly on the Ca/K ratio of the soil solution. When the experimental conditions are properly evaluated, the apparently conflicting results reported concerning the intricate Ca-K relationships in soils and in plants are indeed in fairly good agreement.

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# NITROGEN, PHOSPHORUS, AND POTASSIUM INTER-RELATIONSHIPS IN YOUNG PEACH AND APPLE TREES

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Many field experiments dealing with the mineral requirements of fruit trees have been conducted in various parts of the country on different soil types during the last 25 years. These investigations have shown that apple and peach trees in most fruit-producing areas of the United States made satisfactory growth when supplied with nitrogen in some form. This element, in fact, seemed to be the only nutrient in applied fertilizers to which trees showed a marked response. Other essential mineral nutrients were apparently obtained from the soil in sufficient quantities for optimal growth of the trees. On some of those same orchard soils agronomic crops would not make satisfactory growth without liberal applications of phosphorus and potassium in addition to nitrogen. It is recognized that perennial plants with large and deep root systems may be able to obtain adequate nutrients from the soil or soil solution for satisfactory growth where plants with less extensive root systems may be limited to the available supply in a more restricted area.

In recent years it has been observed that in some regions fruit trees, even though well supplied with nitrogen, have not made satisfactory growth. Peach trees, for example, on some soil types and in certain locations have shown leaf abnormalities, suggesting mineral deficiencies as the probable cause, although orchards showing these deficiencies constitute a small percentage of the total acreage of fruit trees. Some of these orchards are planted on coarse-textured soils such as the sandy and gravelly loams and the leached soils of the Coastal Plain area. More recently leaf scorch of apple leaves similar to that reported by Wallace (15) and found to be due to lack of available potassium in the soil has been observed in a few areas in the eastern part of this country (13). Fruit trees in some sections also have shown leaf-deficiency symptoms as a result of inadequate supplies of some of the minor elements. Little leaf, caused by zinc deficiency (5), and die-back of shoots and internal cork of the fruit, due to boron deficiency, are examples. To a more limited extent magnesium and manganese deficiencies have been observed, particularly on citrus in the Southeast.

Much information on soil-plant relationships has been gained from researches on the intake of nutrient ions by plants in soil, water, and sand cultures. It has been possible to carry many plants through the vegetative and reproductive cycles, determining their mineral requirements and utilization, as well as growth-deficiency symptoms that appeared when nutrients were inadequate during any stage of growth. Much progress also has been made with various quick tests of the soil solution to determine the level of nutrient supply, and with various plant-tissue tests to determine the level of supply within the plant growing on

the soil. This information has been most helpful, particularly with field crops, in interpreting plant response and has served as a basis for fertilizer practices. It has been more difficult to study the mineral requirements of fruit trees during both the vegetative and the reproductive phases of growth, largely because of the size of the trees, the time required to bring the trees into fruit, and the necessity of maintaining requisite environmental conditions for growth and fruiting. Considerable experimental evidence, however, has accumulated in recent years from studies with peach and apple trees in sand culture designed to determine mineral requirements and symptoms of mineral deficiency (3, 4, 6, 8, 9).

In this paper discussion will be confined to some studies that have been made by the authors during the last 6 years on the growth response of young peach and apple trees to varying nutrient levels of N, P, and K in sand culture as related to the amounts of these elements found in the leaves. Establishment of certain quantitative relationships among nutrient supply in the medium, foliar analysis, and tree response would be helpful in studying requirements under field conditions, particularly if leaf analysis could likewise be used as an index of the adequacy of nutrients available to the tree.

#### EFFECT OF NUTRIENT SUPPLY ON GROWTH AND LEAF COMPOSITION

In preliminary experiments, nitrogen levels maintained in sand cultures have ranged from 0 to 168 p.p.m.; phosphorus, from 0 to 93; and potassium, from 0 to 117, with all other elements supplied in adequate and equal concentrations for each series. In these cultures, characteristic growth symptoms resulting from nutrient deficiencies have been studied, and the optimal level for satisfactory growth of 1-year-old trees has been determined. The amounts of nitrogen, phosphorus, and potassium in the leaves of trees receiving various treatments have been determined quantitatively (6, 14, 18).

The most outstanding differences in growth were due to changes in the N level, as shown in table 1. Satisfactory growth of peach trees in sand culture was made only when the N content of the nutrient solution was maintained at 60 or more p.p.m. The green weight of tree produced was much less with minimum levels of N than with low levels of either phosphorus or potassium. Trees adequately supplied with N and P did not show marked reduction in total length of growth even when the nutrient solution contained only 2 p.p.m. of potassium, but characteristic leaf symptoms of K deficiency were apparent and the total weight of growth was lower than that on trees grown with 10 p.p.m. of potassium. Similarly, trees adequately supplied with nitrogen and potassium made satisfactory growth when phosphorus in the nutrient medium was as low as 4 p.p.m. Below this concentration, growth was affected and deficiency symptoms became apparent. The amount of nitrogen, phosphorus, and potassium found in the leaves showed a close correlation with the supply of these three elements in the nutrient solution.

Similar results were obtained with apple trees, as shown in table 2. With increased concentrations from 2 to 60 p.p.m. of nitrogen, growth increased almost

TABLE 1

*Growth of peach trees and composition of leaves as affected by varying amounts of N, P, and K, in nutrient solution*

NUTRIENT SOLUTIONS			AVERAGE TOTAL LENGTH	AVERAGE TREE CIR- CUMFERENCE	TOTAL WEIGHT	LEAF ANALYSIS*		
N	P	K				N	P	K
p.p.m.	p.p.m.	p.p.m.	cm.	cm.	gm.	per cent	per cent	per cent
<i>Nitrogen series</i>								
120	93	117	1032	5.7	615	3.1	0.41	3.1
60	93	117	1169	5.8	589	2.5	0.57	3.5
30	93	117	703	4.5	381	1.9	0.83	3.0
15	93	117	251	3.5	184	2.1	0.96	2.9
<i>Potassium series</i>								
168	93	60	1203	5.8	477	3.1	0.35	2.7
168	93	30	1132	5.7	556	3.3	0.54	1.7
168	93	10	1195	5.3	580	3.3	0.52	0.67
168	93	5	1182	4.7	474	3.0	0.54	0.50
168	93	2	1380	4.5	420	3.0	0.50	0.47
<i>Phosphorus series</i>								
168	40	117	1471	6.2	570	3.1	0.33	2.9
168	20	117	1149	6.1	599	2.9	0.31	3.0
168	10	117	1186	6.1	685	2.9	0.20	2.8
168	4	117	1153	5.9	646	2.5	0.13	2.4
168	2	117	907	4.9	395	2.5	0.11	2.4

\* On dry-weight basis.

TABLE 2

*Effect of different concentrations of N, K, and P on the growth of apple trees*

NITROGEN SERIES*					POTASSIUM SERIES*					PHOSPHORUS SERIES*		
N in nutrient solution	Total linear growth	Green weight of tops	Leaf analysis†		K in nutrient solution	Total linear growth	Green weight of tops	Leaf analysis		P in nutrient solution	Total linear growth	Green weight of tops
			N	K				N	K			
p.p.m.	cm.	gm.	per cent	per cent	p.p.m.	cm.	gm.	per cent	per cent	p.p.m.	cm.	gm.
168	590	341	1.85	2.31	117	590	341	1.85	2.31	93	590	341
60	523	313	1.70	2.35	60	482	314	1.84	1.95	40	601	369
30	351	232	1.39	2.29	30	315	227	1.82	1.69	20	550	355
15	157	106	1.23	2.35	10	254	197	1.81	.83	10	660	365
5	118	51	1.15	1.93	4	149	104	1.78	.68	4	541	349
2	70	34	.94	2.00	2	138	84	1.65	.66	2	292	216
0	62	31	....	....	0	111	51	1.61	.33	0	108	37

\* Total linear growth and green weight of top values represent an average of four trees in each treatment.

† On dry-weight basis.

quantitatively. Increase in growth with concentrations above 60 p.p.m. was less marked. With increasing concentrations of potassium in the nutrient,



growth also was increased, but not so markedly as with nitrogen. Response to phosphorus was similar to that of the peach. Growth was approximately uniform in all series receiving 4 or more p.p.m. of phosphorus. Only when this element was completely lacking in the nutrient, however, did deficiency symptoms occur. Leaf analyses reflected the concentrations of nitrogen, phosphorus, and potassium supplied in the nutrient.

Nutrient levels having been established for optimal growth of peach and apple in sand culture, as well as levels that were inadequate, it seemed desirable to study possible interactions in the nutrient medium of varying concentrations of N, P, and K on growth and possible cause of deficiency symptoms on peaches. For this purpose, concentrations that had been shown to give deficiency symptoms, as well as intermediate concentrations and those that should be adequate, were chosen. Three levels of N (9, 27, and 81 p.p.m.), three of K (3, 10, and 30 p.p.m.), and two of P (2 and 10 p.p.m.) were used. Three trees were grown in sand culture with each of the 18 combinations, and the nutrients were flushed through the sand at regular intervals under time-clock control. Similar experiments have been set up to study the interaction of nitrogen, potassium, and calcium with the phosphorus content adequate and uniform for all combinations.

As in previous experiments the most outstanding differences in growth were those due to nitrogen at the various levels, irrespective of the amounts of other nutrients supplied. With low nitrogen all trees showed reduced growth, with foliage characteristic of nitrogen deficiency. An increase in the nitrogen level resulted in significantly increased growth, even with phosphorus and potassium at their lowest levels, and this increase became greater at the higher levels of phosphorus and potassium. On the other hand, only when nitrogen was supplied at intermediate and adequate levels could phosphorus and potassium deficiencies be noted. Potassium at the levels used showed less direct effect on growth than did nitrogen or phosphorus. No foliar potassium-deficiency symptoms were observed at the lowest levels of either nitrogen or phosphorus, but they were apparent in the low-potassium trees at the intermediate and adequate levels of nitrogen and at the adequate level of phosphorus (16).

The amount of potassium in the leaf increased with increasing concentrations of this element in the nutrient, accumulating in the leaves of trees inadequately supplied with nitrogen for optimal growth and decreasing when the nitrogen content of the nutrient was high and the trees were more vegetative. Thus when nitrogen in the nutrient was maintained at 20 p.p.m., and the potassium supply was adequate (30 p.p.m.), the potassium content of the leaf was around 2.9 per cent on a dry-weight basis, whereas at 85 p.p.m. of nitrogen, and with trees making excellent growth, the potassium content of the leaf dropped to 1.5 per cent.

Calcium showed a similar decrease, though less marked than that of potassium, with increasing concentrations of nitrogen. When both nitrogen and calcium were held at a high level in the nutrient and potassium was at a low level, deficiency symptoms of the latter were more marked than with high nitrogen and lower calcium, though there was little difference in the potassium content of the foliage of trees under the two conditions. The effect of high calcium on the

intake of potassium has been noted by other workers where wide Ca/K ratios were maintained (8).

With 1-year old apple trees, concentrations of nitrogen at 100, 25, and 10 p.p.m., potassium at 100, 10, and 4 p.p.m., and phosphorus at 20 and 2 p.p.m. were used

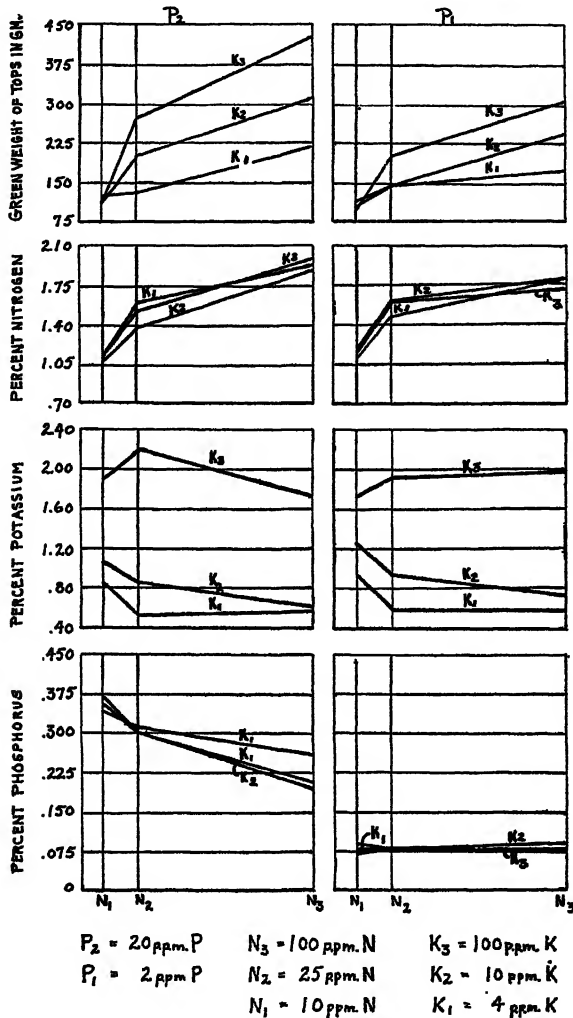


FIG. 1. INTERACTION EFFECTS OF VARYING LEVELS OF NITROGEN, PHOSPHORUS, AND POTASSIUM ON TOP GROWTH AND ON COMPOSITION OF LEAVES OF 1-YEAR-OLD YORK APPLE TREES

Top growth in grams, green weight; leaf composition in per cent, dry weight

in all possible combinations. The 18 different treatments were studied on six trees each (two varieties with three trees each). In all treatments, nutrient elements other than the ones studied were kept at adequate concentrations. The effects on top growth and on composition of the leaves of one variety, the York, are shown in figure 1.

Increasing the concentrations of potassium and phosphorus in the nutrient solution had no significant effect on growth at the low-nitrogen level, but at the medium- and high-nitrogen level growth increased with increasing supply of these elements. No visible potassium- or phosphorus-deficiency symptoms were apparent in any treatment. Increased growth resulted with increased nitrogen supply at all levels of both potassium and phosphorus. With the concentrations used, the lowest level of nitrogen was more limiting to growth than the lowest level of potassium or phosphorus either singly or in combination.

The nitrogen content of the foliage was roughly proportional to the amount supplied in the nutrient solution, particularly under conditions of high-phosphorus supply; the potassium level of the nutrient solution had no significant effect on the nitrogen content of the leaves.

The potassium content of the leaves was directly associated with the amount supplied in the nutrient solution but was also markedly influenced by nitrogen supply. With all three levels of potassium the amount of potassium in the leaves tended to increase with decreasing nitrogen. Phosphorus had no significant effect on potassium content of leaves.

The phosphorus content of the leaves was directly associated with the supply of this element in the nutrient solution, but was also greatly affected by the nitrogen supply in the case of the high-phosphorus treatments. As was true with potassium, the phosphorus content of the foliage increased with decreasing nitrogen. Also in the high-phosphorus treatments the phosphorus content of the foliage tended to increase with decreasing potassium. The phosphorus content of the foliage was not affected by the different potassium and nitrogen treatments at the low phosphorus level.

#### DEFICIENCY SYMPTOMS ON PEACH AND APPLE

##### *Nitrogen*

The characteristic symptoms of nitrogen deficiency have long been recognized in crop plants. These symptoms are not greatly different on the foliage of fruit trees. Nitrogen deficiency was characterized by early cessation of terminal growth and subsequent color changes showing a gradation from green to yellow and progressing along the stem from the oldest to the youngest leaves. Under severe conditions of nitrogen shortage, peach foliage may develop light green spots, which later turn a distinct red, the affected portion abscising and leaving holes surrounded by a red margin of leaf tissue.

##### *Potassium*

The peach appears to be very responsive in exhibiting foliage deficiency symptoms. A number of characteristics seem to hold not only under sand culture but, as will be pointed out later, under field conditions where the potassium level is low. Under low potassium, leaves of the peach are narrow and light green and have a tendency to pucker along the midrib; and under conditions of severe potassium shortage show grayish peppery spots on the leaf, marginal necrosis, and rolling of the leaf blade. Low-potassium trees exhibiting the above symptoms when ade-

quately supplied with nitrogen may make good terminal shoot growth, although the diameter of the shoots will usually be less than that of shoots well supplied with potassium. As indicated in table 1, 1-year-old peach trees receiving 2 p.p.m. of potassium made as much terminal growth as those receiving 60 p.p.m. With the apple, differences in size and color of leaf are not so noticeable, and although 1-year-old apple trees in sand culture require relatively as much potassium as the peach, for satisfactory growth, leaf symptoms are not so marked except where marginal burn or leaf scorch is apparent.

### *Phosphorus*

Symptoms of phosphorus deficiency on the peach are also very marked and in many respects are just the opposite of potassium. The leaf is dark bluish to purplish green but the quality of green differs from the live green of high nitrogen. The leaves show no tendency to roll; the blade is narrow, leathery, and flat; and there is no evidence of puckering along the midrib. These symptoms have been observed only in sand culture and not under field conditions.

### POTASSIUM DEFICIENCY UNDER FIELD CONDITIONS

The discussion thus far has dealt with a study of the response of trees to varying amounts of N, P, and K in sand culture. Conditions for the release of the various bases and cations would be greatly modified under soil conditions where the energy of adsorption and release of ions is greatly affected by the soil complex. Recent studies in this field (1, 10) stress the role played by the colloidal clay particles in the release of important cations such as calcium and potassium.

Studies were made on some 5-year-old peach trees growing in Sassafras gravelly and silt loam soil and showing foliar symptoms of potassium deficiency (7). Nitrogen had been supplied on different plots each year from four different sources; namely, sodium nitrate, potassium nitrate, ammonium sulfate, and cyanamid. Calcium carbonate at the rate of 2,000 pounds per acre had been applied before the trees were set. Trees in all plots except those receiving potassium nitrate showed characteristic though not acute symptoms of potassium shortage. The leaves showed puckering of the laminae along the midrib and tended to roll. Leaf analysis showed a potassium content of 1.5–2.0 per cent for trees receiving potassium nitrate and 0.5 to 0.7 per cent for the other trees receiving equivalent nitrogen from different sources but no added potassium.

The calcium content of the extracted soil solution by rapid test methods showed medium-high content, and quantitative analyses of the leaves showed adequate but not high calcium content. The amount of potassium available to the tree could have been influenced by the Ca/K ratio in the soil. There was an indication that some of the trees fertilized with calcium cyanamid had a lower K leaf content, but the analyses of leaves from trees with deficiency symptoms showed no significant difference between treatments with the different nitrogen carriers. Likewise, there appeared to be no correlation between the pH of the soil and the occurrence of K deficiency. The pH of the soil under trees showing the most acute symptoms ranged from 5.8 in the first foot to 4.8 in the third foot.

All trees showing severe leaf curl regardless of treatment had a K leaf content under 1 per cent. Where potassium nitrate was added the potassium content of the leaf was increased in a 3-year period to an average of 2.6 per cent (table 3). The amount of potassium in the leaves of low-potassium trees varied annually with seasonal conditions and with the amount of fruit borne by the tree. Likewise the potassium content of the leaves was highest early in the year and decreased during the summer. A single sample of leaves taken about midsummer for foliar analysis gave marked differences of K content for low- and high-potassium trees. The growth response of these 5-year-old trees to an adequate nitrogen supply was similar to that of 1-year-old trees in sand culture receiving a nutrient solution high in nitrogen and low in potassium. The leaves of trees fertilized with potassium nitrate were large and dark green with a potassium content of 2 to 2.5 per cent, whereas trees not fertilized with potassium but receiving equivalent amounts of nitrogen were smaller, light green, rolled, and in some instances showed marginal necrosis, with a potassium content of 0.6 to 1.3 per cent.

TABLE 3  
*Potassium content of Elberta peach leaves from fertilizer plots*

TREATMENT	POTASSIUM IN LEAVES		
	1937	1938	1939
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Sodium nitrate.....	0.71	0.99	1.30
Potassium nitrate.....	1.58	2.40	2.65
Ammonium sulfate.....	0.59	1.35	1.32
Calcium cyanamid.....	0.72	1.08	1.09

Experiments have also been carried on with bearing peach trees on a gravelly loam soil low in available potassium where the cover crops had been fertilized annually with 400-500 pounds of 5-8-5 fertilizer (17). The cover crops made excellent growth, but the peach leaves showed symptoms of potassium deficiency, and upon analysis showed 0.75 to 1.2 per cent potassium on a dry-weight basis. When potassium was added either as potassium nitrate or as muriate of potash in a ring application beneath the trees at the rate of 2 to 3 pounds to the tree, normal leaf and twig growth was restored. When leaf samples were collected in midsummer and analyzed for nitrogen, phosphorus, and potassium content, there were marked differences in the potassium content of foliage from fertilized and unfertilized plots (table 4). In this instance the satisfactory growth made by the cover crops could not be used as an index of the supply of available potassium for the trees. The fertilizer applied to the cover crops was drilled in between the tree rows and, though apparently sufficient for cover plant requirements, was inadequate for the needs of the trees. It was only when potassium fertilizers were broadcast under the trees in a ring application that tree growth was improved. One-year-old trees planted on this soil showed more marked symptoms of potassium deficiency than older trees.

It is of interest to note that apple trees on similar soil in an adjacent block did not show recognizable symptoms of potassium deficiency. It has already been pointed out that the potassium requirements for growth of apple trees in sand culture are similar to those of peach trees. Analyses of apple leaves on this soil showed relatively low potassium content (1.0–1.2 per cent) yet significantly higher than that obtained with peaches. This may possibly be due to the fact that the apple through its root system has been able to obtain more potassium from this soil. In general, peach tree growth appears to be more quickly affected than apple tree growth by low potassium under field conditions. Deficiency symptoms appear to be more marked in years of heavy crops than in years of light crops. Reports of the response of stone fruits such as peach, plum, and cherry to potassium have been more numerous than with the apple.

TABLE 4  
*Foliar N, P, and K Content of 9-Year-Old Elberta Peach Trees*  
In percentage of dry weight

ROW	TREATMENT*	ANALYSIS OF PEACH LEAVES		
		N	P	K
6	Cultivation + K around tree.....	3.17	0.18	1.93
7	Cultivation.....	3.04	0.20	0.86
8	Lespedeza + K around tree.....	2.93	0.19	2.12
9	Lespedeza.....	2.79	0.19	0.72
10	Sweet clover + K around tree.....	2.91	0.21	2.28
11	Sweet clover.....	3.13	0.21	1.05
12	Soybeans + K around tree.....	3.20	0.20	2.13
13	Soybeans.....	3.14	0.16	1.02
14	Buckwheat + K around tree.....	3.09	0.18	1.57
15	Buckwheat.....	3.18	0.19	0.71

\* All trees received equivalent amounts of nitrogen in a ring application. The tree middles of all plots received an application of N, P, and K to the cover crops; the trees in even-numbered rows received added potassium as indicated.

Few instances of phosphorus deficiency under field conditions have been reported. If we may judge from the growth of young trees in sand culture, the phosphorus requirement is sufficiently low that fruit trees seem able to obtain adequate amounts for growth even on soils deficient in phosphorus for most annual crops (6, 12). The growth response of the cover crops cannot be taken as an index of the phosphorus requirement of the fruit tree on the same soil.

#### VALUE OF LEAF ANALYSES

In comparing the growth response of 1-year-old trees in sand culture with young and bearing trees growing in soil, it is not inferred that response to equivalent concentrations of ions in the nutrient medium would be the same in the two environments. The availability of these ions to the plant roots would of course be affected by the nature of the soil complex in the proximity of the root zone. In the experiments reported here the amounts of nitrogen, phosphorus, and potas-

sium in the leaves of trees making satisfactory growth have been determined, and in sand culture have been shown to reflect the adequacy of supply in the nutrient solution. This has held true even when fairly wide ratios of concentration, such as N/Ca, K/Ca, and N/P/K, have been maintained. Similarly, under field conditions the amounts of these elements found in the leaves of trees making good growth as well as those in leaves of trees showing deficiency symptoms have been determined. Under orchard conditions it has not been possible to determine the exact concentration of nutrients available in the soil. Once these ions are taken into the plant, however, and enter into metabolic processes resulting in growth, it should be possible to determine the amounts present in the leaves, in the growing tips, or in some other plant part. The values found for N, P, and K should show a relationship to the adequacy of supply in a particular soil environment. When this is done, growth response interpreted through leaf analyses under the two widely varying conditions of environment is very similar, at least with peach and apple trees. Further study is needed to establish relationships with Ca and Mg in order to determine how these and other ions may affect availability and how leaf analysis may be related further to the nutrient supply. In the experiments reported here, leaf analysis has been found to be very helpful in diagnosing growth conditions caused by potassium deficiency in the soil. Thus 1-year-old peach trees in sand culture adequately supplied with nitrogen and all other essential elements except potassium showed leaf deficiency symptoms for that element. Analyses of leaves from the deficient trees showed a potassium content of less than 1 per cent on a dry-weight basis. With increased concentrations of potassium in the nutrient, leaf content increased to 2–2.5 per cent. Samples of leaves from 1-year-old trees growing in the orchard and showing potassium-deficiency symptoms identical with those produced on trees in sand culture had a potassium content of less than 1 per cent on a dry-weight basis. When potassium was added to the soil in a surface application, leaf content was increased the same season to above 2 per cent, and normal leaf and terminal growth were restored. It is of interest also to note that the potassium content of leaves taken from the current season's growth of 8-year-old peach trees in bearing, showing deficiency symptoms, was of the same quantitative order, namely less than 1 per cent on a dry-weight basis.

Leaf analyses have been of great value in determining the potassium level in the leaves of peach and apple trees that have not shown visible evidence of deficiency. Peach trees with small, narrow, light-colored leaves, with a potassium content of 1.25 per cent, have responded to applications of potassium in larger size and darker green color of leaf and in greater diameter of terminal growth. With these changes the potassium content of the leaf was increased to 2.5 per cent. Large dark green leaves from vigorous trees usually have a potassium content above 1.75 per cent. Trees low in potassium may show a leaf content of 1.25 per cent early in the growing season, but by midseason this value may drop to below 1 per cent. As the season advances, trees adequately supplied with potassium will also show a decrease in leaf content, which may be from 2.5 per cent to 1.75 per cent.

The value of 1 per cent has been taken as an arbitrary critical level for peaches and apples, since below this level marked potassium-deficiency symptoms, particularly with peach, usually occur. Since these deficiency symptoms are identified with less certainty in apples, leaf analyses should be a more reliable index of the potassium status in the tree. A recent survey of the potassium content of apple leaves collected from widely scattered orchards in a number of regions showed relatively few orchards with potassium content of leaves below 1 per cent, none of which showed any visible symptoms of potassium deficiency (2). Whether potash fertilization in such orchards would result in increased growth and yield has not yet been determined.

#### SUMMARY

The vegetative growth of peach and apple trees is strikingly affected by lack of adequate supplies of nitrogen in the nutrient solution.

When nitrogen is inadequate, the effects of low phosphorus or low potassium on growth are not so marked, but under a high-nitrogen level growth-deficiency symptoms appear when either phosphorus or potassium is present in low concentration. The deficiency symptoms are more marked in peach than in apple. Potassium-deficiency symptoms on peach are also more noticeable under a high calcium-potassium ratio.

Leaf analyses have shown that the content of nitrogen, phosphorus, and potassium in the leaves is related to the supply in the nutrient in sand culture even when fairly wide ratios of concentrations have been maintained.

Under field conditions, where the available supply of potassium in the soil is low, deficiency symptoms are usually accentuated by adequate nitrogen applications.

Phosphorus deficiency has not been found to any appreciable extent under field conditions. Both peach and apple trees seem to obtain sufficient amounts from the soil to maintain satisfactory growth.

It is believed that the results obtained with leaf analyses justify their further use with fruit trees as an index of the adequacy of available nutrients in the soil and as an aid in diagnosing abnormal growth responses that may be caused by mineral deficiencies.

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# CALCIUM-POTASSIUM RATIOS FOR ALFALFA<sup>1</sup>

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Alfalfa evidently originated in a region where the soil was naturally well supplied with mineral elements. Its North American career began in soils of that type in California. The crop held such promise for the livestock and dairy industries that it rapidly spread eastward and, in so doing, encountered soils that were less and less hospitable to its growth. Although adverse soil conditions can be remedied in large part by the use of lime and fertilizers, the problem of growing alfalfa on the podzolic soils of the eastern states is not a simple one, especially since the plant is a perennial and farmers find it advantageous to keep it growing continuously on the same land for a considerable period of years.

In preparing land for alfalfa, one may follow either of two procedures: first, estimate the mineral requirements of the crop (over and above the amounts the soil on which it is to be grown is capable of supplying) for the entire period of years of its intended growth, and apply them in advance of sowing the seed; second, apply such portion of the crop's requirements at seeding time as is necessary to get the crop well under way, and then add the remainder as top-dressings. In either case there is need to know what amounts and ratios of the nutrient ions are required for optimum growth.

In considering the laboratory phase of this problem, the authors decided to confine their attention first to the Ca-K relationships in soils, since these two elements play particularly large parts in the mineral nutrition of alfalfa. The purpose of the project was to obtain information by the use of which one could predict, from a determination of the content of exchangeable cations in a soil, whether or not the existing amounts of Ca and K and the Ca-K ratio in the exchange complex were optimum for this crop and, if not, how much of either or both of these elements would have to be added to take care of the deficiency.

The optimum Ca-K ratio for alfalfa plants growing in culture solutions, as reported by Lomanitz<sup>3</sup> is relatively narrow. But data so obtained are not directly applicable to field conditions because adsorption, exchange, and fixation reactions occurring in the soil alter the ratios of the available nutrients applied in the form of lime and fertilizers.

Only recently, through the medium of cation-saturated clay colloids, was a method developed for studying ionic relationships in the soil itself as they affect

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<sup>3</sup> Lomanitz, S. 1926 A study of physiological balance for alfalfa in solution cultures. *Soil Sci.* 22: 97-107.

the growth and composition of plants. By such means, Albrecht and McCalla<sup>4</sup> investigated the effect of varying ionic ratios on the delivery of nutrients to plants and their consequent growth and composition. The method permits of controlling the nutrient supply with an accuracy comparable to that obtainable in culture solutions. Accordingly, such a procedure was adopted, the only difference being that in the investigation here reported the soils were prepared from unfractionated topsoil rather than from the colloid alone.

#### MATERIALS AND METHODS

##### *Preparation of homionic soils*

A H-soil, prepared by the Gedroiz method<sup>5</sup> from cultivated Dutchess shale loam, was treated with neutral normal acetates of K and Mg, and with 0.05 N  $H_3PO_4$ , to give K-, Mg-, and P-soils, respectively. A Ca-soil was prepared by titration with the hydroxide. The H-soil had an exchange capacity of 14.6 m.e. per 100 gm. and contained 0.167, 0.838, 1.710, and 0.569 per cent of total Ca, Mg, K, and Na, respectively.

##### *Preparation of soil-sand mixtures*

Six soil-sand mixtures were prepared, in triplicate, from the four homionic soils and from washed quartz sand. The 21 pounds of soil-sand mixture in each pot was made up of  $\frac{1}{2}$  pound Mg-soil;  $\frac{1}{2}$  pound P-soil; 5 pounds of a mixture of Ca- and K-soils so apportioned as to give exchangeable Ca-K equivalent ratios of 1/1, 2/1, 4/1, 8/1, 16/1, and 32/1; and 15 pounds of sand to increase the volume and provide favorable growing conditions for the roots. (Hereinafter the word "exchangeable" will normally be omitted, and the soils will be identified as 1/1, 2/1, etc.) The soil-sand mixtures were placed in uniform glazed pots without drainage outlets. A mixture of 15 pounds of sand and 6 pounds of the untreated original soil was also included in the test.

The salient data for each soil-sand mixture are set forth in table 1. It will be noted that the sums of the Ca and K equivalents in the various combinations are approximately equal. They would have been identical but for the fact that the Ca-soil was less completely saturated than the K-soil. The P-soil contained 0.33 mgm. P per 100 gm. Powdered S and a solution of trace elements were added to each soil mixture at the following rates per 2 million pounds of soil: S, 100 pounds; borax, 20 pounds; and sulfates of Cu, Mn, Zn, and Fe (ferrous), in amounts chemically equivalent to the borax. After the third and sixth harvests, these applications were repeated, that of the trace elements and Fe at the same rate and that of S at the half rate. The soil mixtures were inoculated with a culture of *Thiobacillus thiooxidans*, and with a small amount of a suspension of a fertile soil to restore the normal soil flora.

<sup>4</sup> Albrecht, W. A., and McCalla, T. M. 1938 The colloidal fraction of the soil as a cultural medium. *Amer. Jour. Bot.* 25: 403-407.

<sup>5</sup> Gedroiz, K. K. 1923 The hydrochloric-acid method for determining in the soil the cations present in an adsorbed condition. *Soil Sci.* 16: 473-474.

*Cultural methods*

Thirty inoculated Hardistan alfalfa seeds, containing 0.0091 m.e. K, were planted in each pot, only four of the resulting plants being retained after the first month. The soil was maintained at its optimum moisture content by additions of distilled water. The alfalfa was grown between March, 1941, and May, 1942, and the successive crops were harvested when the plants came into bloom, or when secondary new shoots appeared. The roots were also harvested

TABLE 1  
*Exchangeable cation balance sheet of soils*  
Initial and final cation equivalent ratios and pH values

SOIL	CATION EQUIVALENT RATIOS						INITIAL pH	FINAL pH
	Initial			Final				
	Ca/K	Mg/K	Ca/Mg	Ca/K	Mg/K	Ca/Mg		
1/1	1/1	0.23/1	4.3/1	4/1	1.7/1	2.3/1	6.5	5.2
2/1	2/1	0.35/1	5.7/1	15/1	6.2/1	2.5/1	6.3	5.1
4/1	4/1	0.60/1	6.7/1	103/1	27/1	3.8/1	6.1	4.9
8/1	8/1	1.10/1	7.3/1	131/1	37/1	3.6/1	6.0	5.0
16/1	16/1	2.10/1	7.7/1	112/1	29/1	3.8/1	6.0	5.2
32/1	32/1	4.10/1	7.8/1	714/1	132/1	5.3/1	6.0	5.3
Original	32/1	7.7 /1	4.1/1	181/1	37/1	4.9/1	6.9	6.6

SOIL	CATION CONTENT PER POT*								
	Calcium			Potassium			Magnesium		
	Initial	Final	Remaining	Initial	Final	Remaining	Initial	Final	Remaining
	<i>m.e.</i>	<i>m.e.</i>	<i>per cent</i>	<i>m.e.</i>	<i>m.e.</i>	<i>per cent</i>	<i>m.e.</i>	<i>m.e.</i>	<i>per cent</i>
1/1	157.8	127.3	80.6	157.8	31.67	20.1	36.1	55.4	153
2/1	204.7	158.1	77.3	102.4	10.59	10.3	36.1	63.8	176
4/1	240.4	166.4	69.3	60.2	1.57	2.6	36.1	42.6	117
8/1	263.3	192.7	73.2	32.9	1.47	4.5	36.1	53.9	149
16/1	276.4	212.6	76.9	17.3	1.89	11.0	36.1	55.6	153
32/1	283.3	221.0	78.3	8.85	0.31	3.6	36.1	41.1	113
Original	373.4	283.5	75.9	11.8	1.57	13.4	90.5	58.2	64

\* To translate m.e. per pot to approximate pounds per 2 million pounds of soil, multiply by the following factors: m.e. Ca, by 14.7; m.e. K, by 28.7; m.e. Mg, by 8.9. To convert m.e. per pot to m.e. per 100 gm. soil, multiply by 0.0367.

at the end of the test. The experiment was concluded after the seventh crop, when the average cumulative yield from the best set of triplicate pots had passed that equivalent to 40 tons of dry matter per 2 million pounds of soil. At that point the drain upon the soil nutrients was equivalent to more than 10 years of field cropping with annual yields of 4 tons of hay per acre.

The initial supply of cations in the soil was known, each alfalfa crop was analyzed and its nutrient removal calculated, and the final cation content of the soil was determined at the end of the test. This made it possible to estimate,

with a fair degree of accuracy, the nutrient supply and relationships in the soil at certain intermediate stages in the experiment.

### *Analytical methods*

After drying at 80°C., the harvested material from the triplicate pots was composited and analyzed by the official A.O.A.C. methods. The exchangeable cation content of the soil was determined by the Gedroiz<sup>6</sup> procedure. All cation ratios calculated from analyzes of soils or plants are reported on an equivalent basis.

## RESULTS AND DISCUSSION

### *Alfalfa yields, as related to Ca-K ratios in soil*

The yields, both absolute and relative, for the seven harvests of alfalfa tops and one of roots and the percentages and ratios of Ca and K in the tops and roots are recorded in table 2.

It should be noted immediately that successive yields are not comparable because change in length of day and other uncontrollable factors entered the picture as the seasons advanced. For any one harvest, however, comparisons between yields are permissible, since external factors were identical in their effects and only the differences in the Ca-K ratios were responsible for variations in yield.

One outstanding fact shown by the data in table 2 is that, in the initial harvest, the highest yield was produced on the soil having a Ca-K ratio of 32:1. If the yield from the 1/1 soil is set at 100, that from the 32/1 soil was 138. (It will be noted that the original soil, also having a Ca-K ratio of 32:1, did not produce as high yields as the prepared soil. This may have been because no fertilizer was added to the original soil.)

Consideration of the relationships between the yields at any given harvest and the amounts and ratios of exchangeable Ca and K in the soil will have to be confined to those instances in which the alfalfa plants had removed somewhat less than 100 per cent of the initially exchangeable K, since in the other cases the situation is complicated by the absorption of K from the originally non-exchangeable stores. Some interesting deductions, both as to the amount of exchangeable K and as to the Ca-K ratio in the soil when the yields began to decrease sharply, can be made on this basis.

If it is assumed that, after the first harvest, the amounts of exchangeable cations present in the soil are equal to those initially present (table 1) less those removed (table 3) in the first harvest (and if those present in the roots are disregarded), 264.9 m.e. Ca and 2.9 m.e. K would remain in each pot of 32/1 soil. This is a Ca-K ratio of 91:1. At this point, 67 per cent of the exchangeable K had been removed by the harvested crop. Nevertheless, the relative yield of the second harvest from this soil was 109, and it was not until the third crop,

<sup>6</sup> Gedroiz, K. K. 1931 Exchangeable cations of the soil and plant: I. Relation of plant to certain cations fully saturating the soil exchange complex. *Soil Sci.* 32: 51-62. [See also footnote 5.]

TABLE 2  
Yield, percentage composition, and Ca/K ratio of alfalfa

SOIL	DRY WEIGHT	RELATIVE WEIGHT	Ca	K	Mg	P	S	N	Ca/K
	gm.	✓	per cent	per cent	per cent	per cent	per cent	per cent	
<i>First harvest, June 9, 1941</i>									
1/1	14.65	100	0.77	3.30	0.23	0.37	0.33	2.86	0.45
2/1	17.54	120	1.11	2.66	0.25	0.31	0.35	2.87	0.81
4/1	16.81	115	1.28	2.61	0.29	0.31	0.36	2.89	0.96
8/1	16.97	116	1.52	2.16	0.29	0.30	0.32	2.89	1.37
16/1	17.29	118	1.62	1.69	0.30	0.32	0.33	2.92	1.87
32/1	20.24	138	1.82	1.15	0.34	0.35	0.30	2.98	3.09
Original	10.85	74	1.92	1.12	0.39	0.26	0.34	2.95	3.34
<i>Second harvest, July 19, 1941</i>									
1/1	15.30	100	0.77	3.45	0.23	0.38	0.35	3.04	0.44
2/1	16.33	107	1.04	3.24	0.24	0.36	0.33	2.86	0.63
4/1	16.54	108	1.18	2.97	0.27	0.36	0.33	2.84	0.77
8/1	18.40	120	1.18	2.33	0.27	0.35	0.28	2.71	0.99
16/1	15.60	102	1.54	1.61	0.28	0.43	0.31	2.82	1.87
32/1	16.74	109	1.72	0.85	0.36	0.49	0.28	2.95	3.95
Original	10.44	68	1.44	1.10	0.32	0.24	0.32	2.86	2.56
<i>Third harvest, August 26, 1941</i>									
1/1	16.12	100	0.64	3.06	0.28	0.32	0.30	2.58	0.41
2/1	15.15	94	0.78	2.63	0.26	0.32	0.29	2.46	0.57
4/1	14.37	89	0.95	2.47	0.28	0.32	0.27	2.49	0.75
8/1	18.24	113	1.17	1.52	0.33	0.33	0.26	2.63	1.51
16/1	12.42	77	1.43	1.04	0.36	0.39	0.27	2.82	2.68
32/1	9.54	59	1.53	0.70	0.44	0.50	0.31	3.00	4.26
Original	8.14	51	1.35	0.86	0.47	0.28	0.30	2.89	3.05
<i>Fourth harvest, October 27, 1941</i>									
1/1	16.38	100	0.90	3.54	0.27	0.30	0.34	3.40	0.40
2/1	13.11	80	1.09	3.31	0.28	0.34	0.34	3.40	0.64
4/1	11.43	71	1.32	2.82	0.30	0.35	0.44	3.35	0.91
8/1	13.30	81	1.87	1.30	0.44	0.40	0.37	3.33	2.82
16/1	7.42	45	2.08	0.66	0.55	0.42	0.47	3.56	6.16
32/1	6.40	39	2.21	0.58	0.64	0.54	0.56	3.27	7.44
Original	4.18	26	2.31	0.74	0.63	0.36	0.33	3.52	6.10
<i>Fifth harvest, January 7, 1942</i>									
1/1	14.41	100	1.03	2.90	0.29	0.31	0.23	3.36	0.69
2/1	10.85	75	1.46	2.63	0.32	0.33	0.24	3.25	1.08
4/1	14.52	101	1.83	1.84	0.35	0.30	0.21	3.27	1.94
8/1	6.97	48	2.60	0.90	0.54	0.44	0.23	3.31	5.65
16/1	5.26	37	2.74	0.54	0.64	0.42	0.35	3.57	9.86
32/1	5.10	35	2.55	0.54	0.65	0.47	0.46	3.93	9.14
Original	2.35	16	2.84	0.62	0.56	0.32	0.23	3.25	9.00

TABLE 2—*Continued*

SOIL	DRY WEIGHT	RELATIVE WEIGHT	Ca	K	Mg	P	S	N	Ca/K
	gm.		per cent	per cent	per cent	per cent	per cent	per cent	
<i>Sixth harvest, March 12, 1942</i>									
1/1	22.88	100	0.95	3.33	0.29	0.28	0.20	3.40	0.56
2/1	14.89	65	1.38	3.00	0.31	0.38	0.29	3.67	0.90
4/1	18.26	80	1.96	1.38	0.37	0.35	0.24	3.62	2.78
8/1	9.53	42	2.50	0.77	0.49	0.44	0.26	3.74	6.33
16/1	6.79	30	2.59	0.62	0.54	0.44	0.32	3.77	8.13
32/1	5.76	25	2.69	0.52	0.63	0.51	0.28	4.01	10.05
Original	2.54	11	2.60	1.01	0.53	0.40	0.30	3.92	4.98
<i>Seventh harvest, April 27, 1942</i>									
1/1	24.95	100	0.80	3.35	0.28	0.24	0.31	3.51	0.46
2/1	20.55	82	1.18	2.61	0.29	0.31	0.31	3.64	0.88
4/1	18.81	75	1.72	0.92	0.36	0.30	0.30	3.56	3.64
8/1	9.55	38	2.36	0.52	0.48	0.41	0.47	3.82	8.86
16/1	7.34	29	2.62	0.45	0.50	0.39	0.48	3.89	11.42
32/1	5.80	23	2.57	0.45	0.59	0.46	0.62	4.19	11.10
Original	4.07	16	2.75	0.75	0.62	0.34	0.34	3.84	7.08
<i>Root harvest, April 28-29, 1942</i>									
1/1	37.93	100	0.31	1.04	0.22	0.24	0.15	2.64	0.58
2/1	27.86	73	0.32	0.86	0.21	0.32	0.17	2.60	0.73
4/1	30.49	80	0.42	0.36	0.28	0.29	0.19	2.72	2.28
8/1	17.20	45	0.49	0.21	0.33	0.33	0.25	2.65	4.52
16/1	13.76	36	0.43	0.23	0.32	0.32	0.18	2.62	3.54
32/1	10.42	27	0.47	0.20	0.27	0.38	0.26	2.12	4.58
Original	8.31	22	0.51	0.24	0.26	0.30	0.16	2.19	4.16

after the equivalent of 108 per cent of the original supply of exchangeable K had been removed, that the relative yield fell to 59.

Similarly, the Ca-K ratio of the 4/1 soil was calculated at 30:1 at the beginning of growth of the seventh crop and, by actual analysis, was found to be 103:1 after the last crop and the roots had been harvested. Yet the relative yield of this seventh crop was 75, which is quite satisfactory.

In many ways, however, the data on the 1/1 soil seem most significant. Beginning with the third harvest, the yield on this soil was higher (with one unimportant exception) than that on any other, and the seventh harvest from the 1/1 soil was a record high for all soils and harvests. Similarly, the dry weight of the root system of the alfalfa growing on this soil was 20 per cent greater than that of its nearest competitor. A determination of the exchangeable cations in the 1/1 soil at the end of the test revealed a Ca-K ratio of approximately 4:1. At this point the soil-sand mixture contained 127.3 m.e. exchangeable Ca and 31.67 m.e. exchangeable K per pot.

It is recognized that the content of cations in the exchange complex at any

moment depends not only upon the original supply less that removed in the tops and roots of the alfalfa plants, as previously assumed, but upon that made available from the nonexchangeable stores and that which may have been fixed

TABLE 3

*Milliequivalents, cumulative percentages, and equivalent ratios of exchangeable cations removed from soil by alfalfa*

	MILLIEQUIVALENTS			CUMULATIVE PERCENTAGES			CATION RATIOS		
	Ca	K	Mg	Ca	K	Mg	Ca/K	Mg/K	Ca/Mg
<i>Initial Ca/K Ratio—1:1</i>									
1	5.59	12.36	2.80	3.55	7.84	7.74	0.45	0.23	1.99
2	5.88	13.50	2.88	7.28	16.39	15.72	0.44	0.21	2.02
3	5.13	12.61	3.73	10.53	24.33	26.04	0.41	0.30	1.38
4	7.32	14.83	3.65	15.17	33.78	36.15	0.49	0.25	2.00
5	7.41	10.69	3.43	19.86	40.55	45.63	0.69	0.32	2.16
6	10.85	19.48	5.42	26.73	52.90	60.64	0.56	0.28	2.00
7	9.93	21.37	5.79	33.02	66.45	76.65	0.46	0.27	1.71
Roots	5.89	10.08	6.99	36.75	72.83	95.99	0.58	0.70	0.84
<i>Initial Ca/K Ratio—2:1</i>									
1	9.72	11.93	3.62	4.75	11.65	10.03	0.81	0.32	2.69
2	8.48	13.53	3.25	8.89	24.86	19.03	0.63	0.24	2.60
3	5.87	10.20	3.21	11.76	34.81	27.93	0.57	0.31	1.83
4	7.13	11.10	3.05	15.24	45.65	36.38	0.64	0.27	2.32
5	7.91	7.30	2.88	19.10	52.78	44.36	1.08	0.39	2.74
6	10.26	11.43	3.76	24.11	63.94	54.77	0.90	0.33	2.74
7	12.10	13.72	4.87	30.02	77.34	68.16	0.88	0.35	2.50
Roots	4.48	6.14	4.93	32.21	83.34	81.80	0.73	0.80	0.91
<i>Initial Ca/K Ratio—4:1</i>									
1	10.74	11.22	4.01	4.47	18.64	11.10	0.96	0.36	2.68
2	9.74	12.57	3.66	8.52	39.51	21.24	0.77	0.29	2.66
3	6.78	9.08	3.27	11.34	54.59	30.30	0.75	0.36	2.28
4	7.53	8.24	2.86	14.47	68.28	38.21	0.91	0.35	2.63
5	13.27	6.83	4.14	19.99	79.63	49.69	1.94	0.61	3.20
6	17.87	6.44	5.54	27.42	90.33	65.04	2.78	0.86	3.21
7	16.15	4.43	5.54	34.14	97.68	80.38	3.64	1.25	2.92
Roots	6.41	2.82	6.92	36.81	102.36	99.55	2.28	2.45	0.93
<i>Initial Ca/K Ratio—8:1</i>									
1	12.87	9.38	3.98	4.89	28.50	11.01	1.37	0.42	3.23
2	10.83	10.96	4.12	9.01	61.83	22.41	0.99	0.38	2.64
3	10.65	7.09	4.97	13.05	83.38	36.16	1.51	0.70	2.14
4	12.42	4.42	4.79	17.76	96.82	49.43	2.82	1.06	2.59
5	9.04	1.60	3.07	21.19	101.69	57.92	5.65	1.92	2.94
6	11.89	1.88	3.85	25.71	107.40	65.53	6.33	2.04	3.09
7	11.25	1.27	3.80	29.98	111.26	79.10	8.86	2.99	2.96
Roots	4.17	0.92	4.74	31.56	114.07	92.22	4.53	5.15	0.88

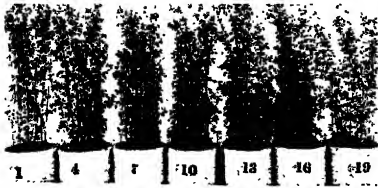


TABLE 3—Continued

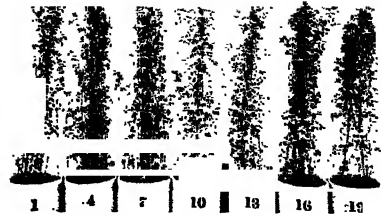
HARVEST	MILLIEQUIVALENTS			CUMULATIVE PERCENTAGES			CATION RATIOS		
	Ca	K	Mg	Ca	K	Mg	Ca/K	Mg/K	Ca/Mg
<i>Initial Ca/K Ratio—16:1</i>									
1	13.97	7.47	4.22	5.06	43.20	11.66	1.87	0.56	3.31
2	11.99	6.42	3.54	9.40	80.33	21.46	1.87	0.55	3.39
3	8.87	3.30	3.71	12.61	99.41	31.73	2.68	1.12	2.39
4	7.70	1.25	3.35	15.40	106.66	41.01	6.16	2.68	2.30
5	7.20	0.73	2.76	18.00	110.86	48.65	9.86	3.78	2.61
6	8.78	1.08	3.00	21.18	117.08	56.95	8.13	2.78	2.93
7	9.60	0.84	3.01	24.65	121.96	65.29	11.42	3.58	3.20
Roots	2.94	0.83	3.64	25.71	126.74	75.30	3.54	4.38	0.81
<i>Initial Ca/K Ratio—32:1</i>									
1	18.38	5.95	5.69	6.49	67.29	15.76	3.09	0.96	3.23
2	14.38	3.64	5.03	11.56	108.42	29.68	3.95	1.32	2.96
3	7.29	1.71	3.47	14.13	127.72	39.28	4.26	2.03	2.10
4	7.06	0.95	3.35	16.62	138.44	48.57	7.44	3.53	2.04
5	6.49	0.71	2.73	18.91	146.42	56.13	9.14	3.85	2.38
6	7.74	0.77	2.97	21.64	155.06	64.35	10.05	3.86	2.61
7	7.44	0.67	2.82	24.26	162.60	72.15	11.10	4.21	2.64
Roots	2.43	0.53	2.32	25.12	168.58	78.58	4.58	4.37	1.05
<i>Original soil</i>									
1	10.40	3.11	3.45	2.78	26.55	3.82	3.34	1.11	3.02
2	7.51	2.94	2.78	4.79	51.65	6.89	2.56	0.94	2.70
3	5.49	1.80	3.16	6.26	67.04	10.38	3.05	1.76	1.74
4	4.82	0.79	2.18	7.55	73.79	12.78	6.10	2.76	2.21
5	3.33	0.37	1.09	8.44	76.98	13.98	9.00	2.95	3.06
6	3.29	0.66	1.11	9.32	82.60	15.21	4.98	1.63	2.96
7	5.58	0.79	2.08	10.82	89.31	17.51	7.08	2.64	2.68
Roots	2.12	0.51	1.80	11.39	93.66	19.50	4.16	3.53	1.16

by the soil. For example, on the 32/1 soil the exchangeable K was augmented to the extent of 72 per cent from that originally non-exchangeable. On the other hand, there appears to have been a slight fixation loss of exchangeable K in the 1/1 soil.

Of great practical interest is the fact that as long as the soil contained adequate supplies of both Ca and K, satisfactory yields were produced at wide ratios of these elements in the soil. Since an equivalent of Ca costs much less than one of K, there would be an economic advantage in maintaining the Ca-K ratio in the soil at 32:1 rather than at some lower level. Furthermore, under such conditions luxury consumption of K would not occur, and unduly heavy losses of this element through crop removal would be avoided. Thus, the percentage K in the first crop on the 1/1 soil was nearly three times that of the first crop on the 32/1 soil. The question to be answered is: If one adjusted the Ca-K ratio in the exchange complex of the original soil in the field to 32:1 at pH 6.5,



FIRST HARVEST, JUNE 9, 1941



SECOND HARVEST, July 19, 1941



THIRD HARVEST, AUGUST 26, 1941



FOURTH HARVEST, OCTOBER 27, 1941



FIFTH HARVEST, JANUARY 7, 1942



SIXTH HARVEST, MARCH 12, 1942



SEVENTH HARVEST, APRIL 27, 1942

*Key to soils*

Pot	Soil
1	1/1
4	2/1
7	4/1
10	8/1
13	16/1
16	32/1
19	Original

FIG. 1. ALFALFA IN REPRESENTATIVE POTS AS IT APPEARED ON HARVEST DATES

in preparation for seeding alfalfa, could the K supply be maintained above the critical point by successive top-dressings with a salt of this element?

In this connection it is necessary to keep in mind that the zones of most rapid depletion of K in the soil are those in the immediate vicinity of the roots, and the K supplies at these locations may not be readily renewable by the top-dressing procedure. On the other hand, the roots in the field are not restricted to pot depth, and the volume of actual soil at their disposal is much greater than it is under greenhouse conditions.

#### *Relation between the Ca-K ratios in the soil and plant*

The data in tables 1 and 2 show that when the supply of both Ca and K in the soil is large and when, with successive crops, the soil Ca-K ratio changes only gradually, the Ca-K ratio in alfalfa tissues remains nearly constant. Thus, on the 1/1 soil there was no essential difference between the 0.77 per cent Ca in the first and 0.80 per cent Ca in the seventh crop; or between the 3.30 per cent K in the first and 3.35 per cent K in the last. The maximum variation in the Ca-K ratio of the tops was between 0.41 and 0.69, although the Ca-K ratio in the soil changed from the initial 1:1 to a final 4:1.

On the 4/1 soil, the Ca-K ratio in the plant tissues was practically constant around 0.9, until the fifth crop. The Ca-K ratio in the soil, at the beginning of growth of the fifth crop, was estimated at 11:1 and, at the end, at 16:1. The Ca-K ratio in the plant tissues of the fifth harvest was 1.94, and this ratio continued to increase to 3.64 for the seventh crop.

Since Ca was present in considerable quantity in all these soils, the Ca-K ratio in the soil increased rapidly as the more easily obtainable K was absorbed and the difficulty of the plant in obtaining K increased. This situation was then sharply reflected in the Ca-K ratios in the plant tissues. Thus, beginning with the second crop on the 32/1 soil, after over 100 per cent of the initially exchangeable K had been removed by the first crop, the Ca-K ratio in the tissues rose successively to 3.95, 4.26, 7.44, 9.14, 10.05, and 11.10 in the consecutive cuttings.

The Ca-K ratios in the roots did not show as much variation as those in the tops. The roots in the 32/1 soil, although permitting of the translocation of Ca and K to the tops of the seventh harvest in the ratio of 11:1, themselves contained these elements in the ratio of  $4\frac{1}{2}$ :1. No doubt the ratio in the roots was a changing value reflecting not only the Ca-K ratio in the soil at the time the roots were removed but Ca-K relationships in soil and plant that had prevailed earlier.

#### *Relationships of Mg, Ca, and K*

The initial exchangeable Mg content was a constant (1.33 m.e. per 100 gm.) for all the prepared soils. The initial Mg-K ratios varied between approximately  $\frac{1}{4}$ :1 and 8:1, and the Ca-Mg ratios between approximately 4:1 and 8:1. The Ca-Mg ratios in the plants were roughly proportional to the Ca-Mg ratios in the soil on which they had grown. In contrast, the Mg-K ratio in the plants showed wide variation, being somewhat similar to that of the Ca-K ratio but never reaching the same magnitude. It is of interest to note that the Mg-K ratio was consistently higher in the roots than in the tops.

*Critical limits*

The evidence on the 32/1 and 1/1 soils indicates that a wide range of Ca-K ratios can exist in the soil without necessarily interfering seriously with the growth of alfalfa. From the data presented, the critical Ca-K ratio might well be placed at about 100:1.

Referring again to the data on the 4/1 soil (table 2), it will be recalled that the relative yield of the seventh harvest was 75, but the evidence strongly indicated that a critical point was approaching and that, if an eighth crop had been grown, the yield would have fallen sharply. The soil at that period contained 1.57 m.e. exchangeable K per pot. This suggests that the critical minimum point for K was probably around 1.5 m.e. per pot. Calculated on the basis of 2 million pounds of soil, this is equivalent to approximately 42 pounds K. At this point about one-half of the supply of K was coming from nonexchangeable sources.

When the Ca-K equivalent ratios in the tops exceeded 4:1, the yields, without exception, were markedly depressed. For example, the ratio in the plants from the 32/1 soil increased from 3.95 at the second harvest to 4.26 at the third. The relative yields were 109 on the second crop and 59 on the third. A knowledge of this critical value should be of use for determining, by tissue tests, the need of alfalfa for K. It was noted, however, that the leaf speckling, which is characteristic of K deficiency, did not appear until after the Ca-K ratio in the tops had become approximately 8:1.

The Ca-K ratios of the tops and roots were nearly identical for the plants growing on the 1/1 and 2/1 soils. This indicates that when an abundance of both elements is present in the soil such a relationship is the normal one.

The highest percentages of Ca and K in the alfalfa tops were 2.84 and 3.54, respectively, and the lowest were 0.64 and 0.45. Whenever the percentage of Ca in the tops of the plants exceeded 2, or the K content fell below 1 per cent, the yields tended to drop abruptly. No critical point in the minimum percentage Ca or maximum percentage K was observed.

*Availability of mineral nutrients*

The cumulative percentage removal of the exchangeable cations is recorded in table 3. A study of these data in conjunction with that part of table 2 showing the cation content of the soil at the end of the test, reveals the following important facts:

An estimated 108 per cent of the exchangeable K was removed from the 32/1 soil in the harvested material of the first two crops. This does not include the K in the roots. During the 13½ months of the test the plants grown on this soil, together with their roots, removed K equivalent to 168.5 per cent of the exchangeable K originally present. Yet the soil still contained 0.31 m.e. exchangeable K, raising the total recovery to 172 per cent. Lesser amounts of nonexchangeable K became available in the 16/1, 8/1, and 4/1 soils.

The amount of Ca which became exchangeable during the test was small and possibly not more than could be accounted for by experimental error. There was a fairly rapid transposition of Mg from the nonexchangeable to the exchangeable state.

*Relation of crop yield to root size, after exhaustion of exchangeable K*

When the initially exchangeable K was depleted and only mineral K was available to the plant, the alfalfa yield fell to a low value which was closely related to the size of the root system. The initial supply of exchangeable K had been largely or entirely exhausted from the 8/1, 16/1, and 32/1 soils at the harvest of the fourth crop (table 3). It seems probable that almost the entire root growth on these three soils was made before the initial supply of exchangeable K had been exhausted, since only the roots from the 1/1, 2/1, and 4/1 soils showed evidence of recent growth when harvested. The weights of roots obtained from the 8/1, 16/1, and 32/1 soils were 17.20, 13.76, and 10.42 gm. respectively. Relatively these are 100, 80, and 60. The relative yields for the fifth crop on these soils was 100, 75, and 73; for the sixth crop, 100, 71, and 60; and for the seventh crop 100, 77, and 61, respectively.

## SUMMARY AND CONCLUSIONS

Hardistan alfalfa was grown through seven consecutive harvests on a series of prepared soils having Ca and K in the exchange complex in initial ratios varying between 1:1 and 32:1, and constant amounts of other major and minor elements. The seven cuttings of alfalfa and the roots were analyzed, and the final content of exchangeable cations in the soil was determined. Nutrient balance sheets were prepared, showing the initial and final cation content of the soil and the amounts of the cations removed in successive crops. The Ca-K, Mg-K, and Ca-Mg equivalent ratios in the soil and plant were calculated.

In general, an abrupt drop in yield occurred when the Ca content of the plant tissue became greater than 2 per cent, when the K content fell below 1 per cent, or when the Ca-K ratio exceeded 4:1, and these may be considered critical limits in this experiment.

It was concluded that alfalfa can adjust itself to wide variations in soil Ca-K ratios, making normal growth at ratios anywhere between 1:1 and 100:1. The highest total yield and the best root development were produced in soil having a Ca-K ratio of 1:1 at the start of the test. The soil having a 4:1 ratio, however, might well be considered more nearly optimum for the period of this experiment, which was designed to have an effect on the soil equivalent to that of 10 years' cropping. On that soil the Ca-K ratio in the test plants was approximately 1:1 for the first crop and a little over  $3\frac{1}{2}$ :1 (well under the estimated critical 4:1 ratio) for the seventh; the content of Ca in the plants never exceeded the estimated critical maximum of 2 per cent; and the amount of K in the plants dropped only slightly below the estimated critical minimum of 1 per cent in the seventh crop. The plants on the 4/1 soil had good root development and showed evidence of recent growth after the seventh crop had been harvested. Although there was some luxury consumption of K by the plants growing on the 4/1 soil, the average percentage K in the harvested crops was only 2.14, which was well below the maximum 3.54 per cent.

# PHYSIOLOGICAL-CHEMICAL FUNCTIONS OF POTASSIUM IN CROP GROWTH

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If water and a comparatively low percentage of ash are excepted, proteins, carbohydrates, and their derivatives comprise the great bulk of the plant. The proportions and amounts of these constituents are often intimately associated with the relative degree of vegetative and reproductive vigor. Accordingly, possible influences of potassium on the nitrogen and carbohydrate content of the plant should be considered along with other functions of potassium.

Of the several different forms of nitrogen that plants can freely absorb, nitrate is the only one considered here, for regardless of the type of nitrogenous fertilizer employed, it is the chief external source of nitrogen available to crop plants in the field (5). The quantity of nitrate available for any given functional level of the plant is of extreme importance in crop production. For best economic results, there should be neither an excess nor a deficiency in relation to carbohydrates. In practical pineapple culture it has been found profitable to adjust the nitrate supply in the plant on the basis of the concentration of carbohydrates (5).

## NITRATE AND CARBOHYDRATES

For maximum production of pineapples, the nitrogen requirement per acre has been found to vary by as much as 75 per cent in successive years on virtually the same site (6). This is due, in large part, to variation in climatological conditions that influence carbohydrate synthesis. A very low concentration of nitrate in the pineapple plant is adequate for maximum possible fruit production when carbohydrates are low. In contrast, when carbohydrates are high, yields are seriously reduced unless the plants are kept essentially filled to capacity with nitrate.

Nitrate in itself does not materially affect the growth responses of plants. Nitrate reduction, oxidation of carbohydrates or their derivatives, and new protein synthesis must first occur. If plants do not have an adequate carbohydrate reserve, nitrate reduction ordinarily takes place only very slowly and may lead to still further carbohydrate deficiency. In contrast, plants high in carbohydrates reduce nitrate and synthesize new proteins with extraordinary vigor (5). If maximum potentialities are to be realized in fruit production such plants must contain a very liberal reserve of nitrate.

## POTASSIUM AND NITRATE ABSORPTION

Thus in nitrogen nutrition it is of the utmost practical importance to regulate advantageously the nitrate reserves in the plant. In this endeavor potassium plays an essential role, for the absorption of anions, such as nitrate, is greatly accelerated in many plants by the presence of rapidly absorbable cations such as

potassium and calcium (1, 7, 10, 11, 12, 13). Pineapple plants, for example, do not absorb nitrate freely under field conditions in Hawaii, when the potassium supply is low. This relationship is not apparent, however, in all species of plants under all circumstances, because many other factors may be dominant in relation to intake of nitrate. Moreover, even under conditions of extreme potassium deficiency, plants of a kind that store nitrate may become filled to capacity with it, particularly where sodium is substituted for potassium (4, 12). However, this apparently is not because of a high rate of absorption of nitrate but rather is correlated with very limited increase in volume of the plants, which grow little if the potassium supply is seriously curtailed. In pineapple culture in Hawaii there appears to be no practical substitute for potassium in its role in facilitating absorption of nitrate.

It has been emphasized that the required level of nitrate nutrition of pineapple varies with opportunity for carbohydrate accumulation. Likewise the amount of potash that may be required will vary with weather conditions from year to year. Experiments indicate that under all conditions, a certain minimum concentration of potassium in the pineapple plant is essential. But when carbohydrates are high, and relatively much nitrate is therefore needed, additional potassium, beyond that required for other functions, is necessary for nitrate absorption (7). There must, of course, be an external supply of nitrate, but as a practical procedure, potash when needed is now applied to pineapple fields in part to increase absorption of nitrate.

#### POTASSIUM AND NITRATE REDUCTION

In addition to its effect on absorption of nitrate, there is considerable experimental evidence in the literature (1, 6, 10, 11, 12, 13, 14) to indicate that directly or indirectly potassium is essential for reduction of nitrate and perhaps for later stages of protein synthesis. A fairly convincing demonstration of the apparent relationship of potassium to nitrate reduction appears to have been furnished by potassium-deficient tomato plants with which the writer was working some years ago (4). Ordinarily nitrite is not found in tomato plants except following a sudden flush of nitrate reduction (5). These potassium-deficient plants, as usual, contained no nitrite, but reserves of nitrate and carbohydrates were present. The latter accumulated only during the early stages of potassium deficiency, apparently because but little protein was synthesized. When the plants were shifted to a nutrient solution containing abundant potassium, the nutrient was rapidly absorbed and translocated to all parts of the plants, a very characteristic response, as recently brought out by Overstreet and Broyer (8). This was shortly followed by the appearance, for a brief period only, of strikingly high concentrations of nitrite. Though similar manipulation of phosphorus-deficient plants from low to high phosphate culture will also often result in formation of nitrite, it would seem that potassium, along with other elements, must be very intimately associated with at least the early stages of synthesis of protein from nitrate.

As new proteins are synthesized from nitrate, carbohydrates are utilized in the process. In that potassium apparently favors protein manufacture, it thus

makes for relatively rapid use of carbohydrates. This would not be expected to be disadvantageous, however, unless the plant contained an excessive reserve of nitrate in relation to carbohydrates. Certainly the practical indication is to apply enough potash but to avoid an excess of nitrate. Failure to follow this procedure may result in overvegetative pineapple plants and in a delay of several months in time of harvest of fruit (7). Although low temperature apparently often in large measure controls time of blossom-bud differentiation in pineapple and other plants, and the photoperiod in some species is a determining factor, plant composition, in many instances, is closely correlated with time of blossoming and with other phases of plant performance.

For example, Russell (9) reports that potassium in its practical effect on plants is the counterpart of nitrogen and that the two elements are intimately linked in their action. Hepler and Kraybill (2) found that high-potash fertilization delayed the date of blooming of tomatoes. These typical responses to a high level of potassium nutrition, when coupled with abundant nitrate, are probably correlated with a comparatively high rate of nitrate absorption and reduction and new protein synthesis, which, under some environmental influences might lead to relatively low carbohydrate reserves and the characteristic plant responses noted.

#### POTASSIUM AND CARBOHYDRATE RESERVES

Although potassium does apparently accelerate absorption and reduction of nitrate, with concomitant oxidation of carbohydrates or their derivatives, evidence in the literature shows that, directly or indirectly, potassium along with other elements is an important factor in  $\text{CO}_2$  assimilation (1, 4, 10, 11, 12, 13, 14). Experiments with pineapple have indicated repeatedly that, when adequately supplied with potassium reserves, the plants were materially higher in carbohydrates than were others deficient in this element (7). This has been true even though the former, under field conditions, have been typically much higher in nitrate, because of the favorable effect of potassium on nitrate absorption already mentioned. Thus, coupled with higher reserves of both nitrate and carbohydrates, the high-potassium plants have been larger and have greatly out-yielded others that were deficient in this element. As Russell points out, the effect of potash in apparently bringing about more efficient photosynthesis is often to correct the adverse effects, on fruit production, of an excess of nitrogen (9).

#### SELF-ADJUSTMENT OF PLANT TO MULTIPLE DEFICIENCIES

The role that potassium apparently plays in relation to nitrate and  $\text{CO}_2$  nutrition seems further emphasized by responses of pineapple plants in experimental plots (7). In many tests in areas where soil potassium is low, fertilizer treatments that are not extreme or much out of the range of practical productivity have resulted in considerable increases in size of fruit and in yields from added potash. On the other hand, differences in quality of fruit between treatments, harvested on the same day, have usually been negligible with respect to such factors as color and texture of the flesh, and content of sugars and acids. In turn, except for differences in plant size, the various levels of potash fertilization



have typically produced little or no noticeable effect on appearance of roots, stems, and leaves.

Lack of apparent difference, between the treatments employed, in quality of plant or fruit, was apparently associated with the fact that, when potassium reserves were low in the plant, a condition of proximately balanced multiple deficiencies was seemingly displayed. It is notable that the high-potassium plants contained relatively high concentrations of carbohydrates. This was presumably due to the favorable influences of potassium upon  $\text{CO}_2$  assimilation previously discussed. But, as already emphasized, under field conditions in Hawaii, potassium markedly increases absorption and assimilation of nitrate by the pineapple plant. As might be anticipated, therefore, the potash-fertilized plants were found to be not only high in carbohydrates but high in nitrate as well. In contrast, in the plots where volume of growth and yield of fruit were materially curtailed by lack of adequate potash fertilization, the reserve of carbohydrates was much lower. Nevertheless, because absorption of nitrate was apparently also limited by lack of potassium, even though nitrogen fertilization was the same in all treatments, a proximate balance perhaps resulted between nitrate and carbohydrates, with both on a comparatively low plane as compared to the potash-supplied plants.

Some Hawaiian soils low in potassium are also low in phosphorus. Many pineapple plants lacking an adequate supply of potash absorbed phosphate comparatively freely even in soils that were very low in phosphorus and unfertilized with it. This was apparently because nitrate exerted a strong repressive action on phosphate absorption. The potassium-deficient plants, being comparatively low in nitrate, were thus able to absorb phosphate freely. In contrast, potash-fertilized plants, being higher in nitrate, were relatively low in phosphorus content, except where this element was present in abundance in the soil or was added to it as a fertilizer.

The foregoing statements indicate very briefly certain compensating interrelationships that are frequently found in pineapple fields. Other situations often arise, which become understandable only through frequent quantitative records of growth and chemical composition of plants. There is no single common factor that can be employed as a guide for potash applications, unless it is the plant itself, which supplies an integration of all environmental influences. For instance a case which would seemingly be at variance to some of the plant responses just described, but which actually is in much the same category, is furnished by pineapple plants growing in soils low in potassium but not in phosphorus. Under such circumstances added potash increases yields, as would be expected. On the other hand, phosphate fertilization, even though not directly needed, sometimes increases yields. In contrast, potash and phosphate additions together may give no greater fruit production than either alone.

Studies of interrelationships of nutrient ions (1, 7, 10, 11, 12, 13) have demonstrated that under some circumstances phosphate as well as nitrate favors absorption of potassium. Therefore phosphate fertilization, even though not directly required, may be associated with increased intake of potassium. Of course the reverse situation might possibly occur, as potassium would be ex-

## POTASSIUM IN CROP GROWTH

pected to contribute to greater absorption of phosphate and nitrate. With relatively free intake of nitrate, however, phosphate absorption is invariably repressed in pineapple. That responses of this nature in the field are not peculiar to pineapple is indicated by Lilleland and Brown (3), who say in part, concerning their work with peach trees, "potassium was increased in the leaf by applications of phosphorus . . . . Growth increases in 1938 and 1939 could be correlated with potassium [in the leaves], although no potassium had ever been added."

### POTASSIUM AND STRUCTURE OF STEMS

There is an enormous volume of literature dealing with influences of potassium upon structure of stems. Much of this is concerned with work done on grains to determine influences of potassium upon stiffness of straw. Almost without exception this work is considered solely on the basis of the potash treatment of the plants. Any effect on the carbohydrate content of the plant, as brought about by seasonal conditions or treatments imposed, is seldom considered. Plant descriptions in the literature and extensive personal observations over several years on many different crops leave room for little doubt, however, that stiff straw is most frequently obtained when carbohydrates are abundant. As already brought out, carbohydrates tend to accumulate most readily when the nitrate supply is not excessive and conditions are favorable for  $\text{CO}_2$  assimilation. Potassium is frequently recorded as favoring the development of thick cell walls and stiff straw, but in perhaps as many cases this element is reported as having the opposite effect (4). Clearly, structural elements of lignin or cellulose, which represent carbohydrates in the most condensed form, cannot become highly developed under conditions of carbohydrate deficiency. As in fruit production, the practical answer is to apply enough potash but to regulate nitrate reserves on the basis of carbohydrate content.

It has been emphasized that, directly or indirectly, potassium is essential for carbohydrate synthesis and therefore it is obviously important in relation to cell wall formation and stiffness of stems. On the other hand if nitrate reserves are high in relation to carbohydrates and if carbohydrates are not replenished through photosynthesis, at a rate that exceeds their utilization in respiration and protein manufacture, cell walls will be thin and stems structurally weak even though the plants contain an abundance of potassium. Although this element is an important factor in  $\text{CO}_2$  assimilation, it is only one of many that may limit carbohydrate accumulation and consequently cell wall thickness and stiffness of stems.

### POTASSIUM AND CELL DIVISION

Except for simple salts of organic acids, it is not known that potassium enters into any organic combinations in the plant. Moreover, it is freely translocated from mature to meristematic tissues when there is a deficiency of it. Further, when developing fruits are present it is often in large part transferred to them, with subsequent death of vegetative growing points. These facts have been brought out by many workers, who have consistently emphasized the importance of potassium in the cambium and in other actively growing tissues (4). Lack of

potassium may therefore drastically modify plant form. This is true not only of aerial organs, but even more particularly of storage structures, such as sweet potatoes or beets. When potassium is insufficient for development of cambium-like tissues of the sweet potato, for example, it is translocated from such structures to the embryonic tip of the storage root, and the potatoes therefore increase in length but little in diameter.

These adverse influences of potassium deficiency on plant form are not peculiar to a lack of this element. Nitrogen deficiency will bring about much the same result, as would probably a lack of other comparatively mobile elements that are essential for cell division. Potassium is important in its buffer relationship; it often favors absorption of nitrate; it plays a dominant part, directly or indirectly, in protein and carbohydrate metabolism; but more specific information seems to be lacking. Overstreet and Broyer (8) have recently been tracing the movement of this element with radioactive potassium. Possibly by employing this technique, coupled with analyses for definite chemical bodies and purposeful experimental manipulation, more specific information can be obtained. This would be in contrast to experiments with various levels of potassium where chemical analyses of plants have been limited chiefly to empirical fractions of nitrogenous and carbohydrate constituents.

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# THE BEARING OF POTASSIUM ON THE QUALITY OF TOBACCO

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The production of tobacco of high quality is influenced by many factors, among which are the absorption and the utilization of nitrogen and potassium. That these two nutrients profoundly affect the character of growth has long been known, but their role in the production of high-yielding, disease-resistant tobacco of excellent quality is frequently misunderstood.

Many investigators have attributed the lack of resistance to leaf spot diseases in tobacco to excessive nitrogen uptake, but some of the most seriously diseased samples examined in these laboratories have been found to contain considerably less than the normal nitrogen content of the variety. Disease-free tobacco grown on adjacent plots has been found, on the other hand, to possess as a rule the normal nitrogen content of the type.

Certain investigators have attributed disease resistance to adequate potassium uptake, whereas others in recent years have denied that any relation exists between potash fertilization and disease resistance.

The assumption that the three factors, excellence in quality, resistance to leaf spot diseases, and economic yield are incompatible is common among growers of tobacco, although some growers succeed in combining quality and resistance with satisfactory yield year after year.

These conflicts in opinion and the lack of evidence to explain apparent discrepancies in observation led the authors to initiate a research program in this field. This has been conducted for more than five years through plot work, seedbed studies, greenhouse experiments, and chemical and bacteriological laboratory investigations. Extensive field surveys also have been made to gather further data. Data obtained in this program and conclusions drawn therefrom which pertain to the bearing of potassium on quality, yield, and disease resistance are presented briefly in this paper.

In the production of tobacco there are two distinct phases in the culture of the plant in which environmental conditions and cultural practices differ markedly. Seedlings are produced in coldframes, hotbeds, or greenhouses and later are transplanted to the field. Investigation of the culture of the crop, therefore, has been divided into separate studies of tobacco in the seedbed and in the field.

## SEEDBED INVESTIGATIONS

In its accepted meaning, "quality" in the seedling has usually covered disease resistance. The quality seedling is free from disease, transplants without great loss, and strikes root readily even under somewhat adverse conditions in the field. "Yield" in the seedbed usually refers to two factors: number of plants produced per square foot of bed, and length of time required to produce a plant suitable for setting in the field.

Thirty years ago the practice of seedbed steaming was introduced in the Pennsylvania tobacco-producing region, and within a few years this method supplanted all others in the preparation of tobacco seedbeds. Although designed to destroy weed seeds, steaming was soon recommended as a necessary sanitary precaution in the fight against seedbed diseases. These diseases became an economic problem in the years immediately following the introduction of seedbed steaming.

Surveys, by the authors, of the tobacco region of Pennsylvania have shown that it has been the practice to incorporate large amounts of fresh manure and large applications of cottonseed meal usually without P and K supplements in the soil prior to steaming. The bed was then steamed and seeded within a short time. The appearance of leaf spot diseases in such beds was the rule, and the plant produced might well be described as soft, succulent, root-deficient, mineral-starved, and nitrogen-gorged. In order to maintain sufficient moisture in the upper layer of freshly steamed heavy soil, it was necessary to water daily and keep the bed tightly covered with cloth to prevent evaporation. An examination of the soil usually showed a uniformly high content of  $\text{NH}_3$ -nitrogen, little  $\text{NO}_3$ -nitrogen, a water-logged condition, and excessive reproduction of bacteria within the soil and on the aerial parts of the seedling.

All seedbed soils and all seedling plants examined showed the presence of the bacteria associated with the leaf spot diseases of tobacco regardless of sanitary precautions taken by the grower and regardless of the presence or absence of visible signs of disease.

At this stage in the investigation the authors and their associates made a study of the nature of these bacteria and established that these organisms, *Phytophthora tabaca* and *P. angulata*, were merely transitory physiological adaptations of the ubiquitous soil saprophyte, *Pseudomonas fluorescens*. It was further established that these organisms are not destroyed in seedbed steaming or by other routine sanitary measures followed in the Pennsylvania tobacco area and that the normal tobacco plant is exposed to these adaptations of *Pseudomonas fluorescens* at all times in both seedbed and field<sup>1</sup>.

It became evident as a result of the information obtained in this phase of the investigation that the incidence of leaf spot diseases is related not to the presence of the organisms (which are ubiquitous) but rather to the relative resistance of the host to infection.

An investigation of the factors controlling resistance to leaf spot diseases in the seedbed has shown that the tilth and moisture-holding capacity of the soil must be excellent in order to produce a plant with adequate root system and with the minimum use of water. In addition the nutrients supplied must be available in such proportions that the N/K ratio of the seedling is approximately 0.6. Furthermore, beds must be ventilated and photosynthesis must be undisturbed by excessive use of cloth. Under such conditions high-quality, disease-resistant seedlings may be produced economically.

<sup>1</sup>Reid, J. J., et al. 1942 Bacterial leafspots of Pennsylvania tobacco. Pa. Agr. Exp. Sta. Bul. 422.

The provision of such environmental conditions is not difficult. Fall-steaming of the previously manured bed permits a return of the soil to approximately normal physical condition through alternate freezing and thawing in the winter months. This eliminates much of the trouble. It is not necessary to water fall-steamed beds excessively or to keep them closed in order to hold moisture. Fall-steaming coupled with suitable fertilization to permit the uptake of sufficient K and other minerals results in the production of high-quality disease-free plants. It has been found that an application of a 4-8-12 or closely allied fertilizer mixture at the rate of 1,000 pounds per acre will suffice for the nutrient requirements of the seedlings.

It is true that there is a definite limit to the number of quality seedlings that can be produced in a given area, and the grower may seed too heavily in an effort to provide more seedlings than the bed space warrants. To this extent quality and excessive plant yield in the bed are incompatible. On the other hand, the difference in seedling size often noted when soft succulent plants are contrasted with normal high-quality plants is more apparent than real. Laboratory studies show that the weight of dry matter produced by the quality plant is as great as that produced by the tall, stringy, succulent one.

#### FIELD CULTURE OF TOBACCO

In the investigations of field culture of tobacco conducted by the authors, the cooperation of the Chatham Substation of the Virginia Agricultural Experiment Station was obtained. As a result, the research included the field production of Pennsylvania tobacco of the cigar-filler type and also the flue-cured tobacco of Virginia. The aid of leaf experts in the industry was enlisted, and their judgment of quality was obtained on all samples handled. More than 500 samples of flue-cured tobacco and more than 1,000 samples of cigar-leaf tobacco were examined in the chemical and bacteriological laboratories in the course of these investigations. Determinations of the N and K content and of the microflora were made routinely, and in addition, as circumstances warranted, determinations were made of Ca, protein N, nicotine, reducing sugars, steam-volatile acids, and fixed organic acids. These chemical and bacteriological data were related directly to quality in the leaf.

The results showed that flue-cured tobacco of excellent quality contains approximately 2 per cent N, at least 2 per cent K, and 18 to 25 per cent reducing sugars. Any significant divergence from these values was found to be reflected in a lowering of the quality of the leaf.

High-quality cigar-leaf tobacco was found to contain between 3.5 and 4.2 per cent N, slightly more K than N, decidedly less Ca than K, and at maturity, protein N somewhat in excess of nonprotein N. It was also found at maturity to contain somewhat less than 1 per cent of oxalic acid, from 8 to 12 per cent malic acid, and about 2.5 per cent citric acid. These values change during air-curing, but any serious divergence at maturity was associated with lack of quality.

The microflora of flue-cured tobacco was found to be an excellent index of

quality, high quality being associated with an active saccharolytic flora, and poor quality with either a proteolytic or inert flora depending on the factors responsible for the lack of quality. In a somewhat similar manner the bacteriological findings in the case of cigar-leaf tobacco were related to the quality.

With this information on the relation of quality to chemical composition and microflora of the leaf as a reference point, attention was turned to the study of fertilizer experiments at Chatham, Virginia, and Roseville, Pennsylvania.

The Chatham studies<sup>2</sup> revealed that under the conditions of the experiment the highest-quality leaf was obtained by the use of three to four units of potash for each unit of nitrogen applied. Typical analytical data on tobacco leaves from a high-quality plot follow:

YEAR	NITROGEN	POTASSIUM	REDUCING SUGARS
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
1938	2.07	2.17	22.18
1939	1.93	2.43	22.58

Throughout a 4-year study of these plots it was found that smaller applications of potash resulted in a lowering of quality, of market value per acre, and of K and reducing-sugar content and an increase in nitrogen content, although nitrogen additions were the same in all plots in the series. Larger applications of potash resulted in a slightly lower N content, a slightly higher K content, with but little change in reducing sugar content, and slightly less monetary return per acre.

Tobacco grown with three or more units of  $K_2O$  per unit of N was uniformly free from leaf spots of all types during the course of the study, although those plots receiving less  $K_2O$  exhibited leaf spots physiological and bacterial in nature.

The studies of the Chatham tobacco included separate analyses of lower, middle, and upper leaves from each of the plots included in the program. This revealed a significant fact in the chemical composition of the plant. All treatments with less than three units of  $K_2O$  per unit of N resulted in the production of a plant with less potassium in the lower leaves than in the upper part of the plant. This condition was always found to be associated with inferior quality not only in the K-deficient lower leaves but in the upper leaves as well. Treatments giving the highest quality resulted in a uniform distribution of potassium throughout the leaves. Excessive  $K_2O$  fertilization resulted in a greater accumulation of K in the lower leaves than in the middle and upper leaves. It would appear, therefore, that potassium deficiency actually exists in any tobacco plant that contains at maturity less potassium in the lower leaves than in the middle and upper leaves and that such deficiency is associated with a definite lack of quality in all leaves of the plant. This work indicates that such a deficiency is also associated with susceptibility to leaf spotting, which is frequently economic in severity.

<sup>2</sup> Gribbins, M. F., Reid, J. J., and Haley, D. E. 1941 The distribution of potassium in bright leaf cigarette tobacco and its influence on the quality of the leaf. *Jour. Agr. Res.* 63: 31-39.

The problems confronting the grower of cigar-leaf tobacco on the heavy soils of Lancaster County, Pennsylvania, differ from those of the Virginia grower of flue-cured tobacco. The yield of cigar-filler leaf must be far larger in terms of pounds produced per acre than in the case of flue-cured tobacco, if a profit is to be realized. In addition the cigar leaf must contain approximately twice as much nitrogen and potassium as does the flue-cured leaf. In order to obtain large yields of the cigar-leaf tobacco, either heavy applications of animal manure or extensive green manuring supplements the use of commercial fertilizers on most tobacco land. Outbreaks of leaf spot diseases have constituted an ever-present threat to the Pennsylvania crop during the last 25 years, and yield and quality on the average farm have varied greatly with climatic conditions obtaining from year to year.

Dry-weather crops of cigar-leaf tobacco are poor in quality, and the leaf is heavy, gummy, and difficult to ferment. Potassium content is usually low and Ca content high. Yields are not satisfactory in these dry seasons, but disease in economic proportions does not appear. The crop of 1929 is an example of such tobacco.

Wet-season crops, although not of the best, are superior in quality to dry-season crops, but the leaf is thin and the yield is not always satisfactory. Contrary to popular opinion, disease is of little significance in wet seasons if there has been sufficient moisture to maintain growth at all times. The crop of 1942 furnishes an excellent example of tobacco produced in a truly wet season.

Seasons in which the amount of rainfall is ideal and distribution equitable are infrequent, but the crop of 1936 furnishes an example of tobacco produced under such conditions. Yields are large, quality is good under proper fertilization, the leaf ferments well, and the chemical composition shows K in excess of N in the best of the crop. Leaf spot disorders do not occur in such years.

The season of erratic rainfall distribution with periods of drought and periods of excessive rainfall interspersed constitutes the fourth and perhaps the most prevalent type. These conditions result in inferior quality in the bulk of the crop, often poor burn and poor fermentability, and widespread loss from leaf spot diseases. Such tobacco is relatively high in nitrogen and low in potassium and contains abnormally large amounts of calcium and oxalic acid.

In spite of these wide fluctuations in the bulk of the Pennsylvania crop due to climatic conditions from season to season, some growers year after year produce good tobacco with good yields and no economic loss from disease. Likewise, on certain plots of the Pennsylvania Agricultural Experiment Station similar tobacco has been produced, although adjoining plots yielded small amounts of inferior leaf, riddled in many cases with leaf spot diseases.

On the basis of this knowledge, extensive surveys were made by the authors and additional plot work was undertaken. Having previously determined that the bacteria associated with leaf spots constituted a normal part of the plant flora and that leaf spot incidence, therefore, was in no way related to the mere presence of the epiphyte, the authors were in a position to study the epidemiology of the leaf spot diseases to determine why certain plants succumbed while others lived in health with the organism as a harmless saprophyte on the leaf.



From the field surveys and chemical analyses of tobacco procured from growers in addition to crops from the experimental plots it was evident that disease resistance invariably accompanied excellence in quality and that such tobacco contained at least as much K as N. On the other hand, this information could not be directly related to K fertilization, as many plots and fields heavily fertilized with K failed to produce either high quality or disease resistance under erratic rainfall. Chemical analyses showed, however, that these plants had failed to assimilate adequate amounts of K, although tests showed its availability in the soil at the end of the growing season. For example, plots in the 4-year rotation in 1937 which received at least 1,000 pounds per acre of a 3-8-12 fertilizer yielded tobacco of high quality and with insignificant leaf spotting, whereas plots in the 3-year rotation with equivalent fertilization suffered more than 20 per cent loss from leaf spot diseases and the tobacco remaining was poor in quality and yield. Analyses revealed that the tobacco in the 4-year rotation had taken up almost as much K as N whereas that in the 3-year rotation had absorbed only about half as much K as N. Examination of root systems showed that the plants on the 4-year rotation had developed almost normally, whereas the roots of the plants of the 3-year rotation plots were much less extensive. The initial handicap of the soil under the two systems of rotation was determined by a study of the check plots and is very pertinent to the entire problem. These data are briefly summarized as follows:

ROTATION	NATURE OF LAND	LEAF SPOT DAMAGE	YIELD PER ACRE	SALABLE TOBACCO PER ACRE
		<i>per cent</i>	<i>lbs.</i>	<i>lbs</i>
4-year	Untreated corn land	11.9	1008	888
3-year	Untreated clover land	31.2	1092	751
3-year	Untreated alfalfa land	35.7	1176	756

It is obvious from these data that a given treatment had a much greater handicap to overcome on the legume sodland than on the stalkland.

Further plot studies, based on this information, showed that in those years of erratic precipitation with drought followed by excessive rainfall, the tobacco plant deteriorated in quality and in disease resistance in accordance with the extent to which it suffered from interruptions in growth followed by tremendous N uptake at the break in the drought. Physiological youth of some plants would save them from disaster whereas those undergoing such interruptions while physiologically old invariably suffered severely. Soil drainage, tilth, rotation, manurial treatments, and cultivation as well as commercial fertilization determine the extent to which a plant may continue to grow and develop normally under adverse conditions.

For proper tilth and moisture-holding capacity in the heavy soils of Lancaster County, Pennsylvania, a liberal supply of humus is necessary. This need cannot be met by the incorporation of old plant residues or of fresh animal manures if there is insufficient moisture to accomplish the conversion of this raw material

to humus. The plant living over a bed of fermenting organic material is usually suffering from microbial competition not only for moisture, if rainfall is scant, but also, in the early stages of growth, for nitrogen if the organic material is deficient in readily available nitrogen. Far from supplying the moisture-holding capacity of humus, these raw materials actually act in the opposite direction until humification has been accomplished in large measure.

The solution to the question of the lack of proper nutrient absorption by tobacco on old legume sodland in years of erratic precipitation is, therefore, a simple one. Such soil does not provide a moisture reserve for uninterrupted growth. Moreover, it contributes the most N to the plant not when needed in such seasons but rather when the plant is unable to take care of excessive N absorption. On a soil manured with unfermented animal manure, fermentation is somewhat more readily accomplished and N deficiency in the early part of the season is less likely to occur.

Further investigations have shown that any condition which restricts root development or deprives a plant of sufficient moisture in time of drought leads to growth interruption, poor K uptake, N uptake at the wrong period, inferior quality, and susceptibility to disease.

In order to ensure utilization of applied potassium, with consequent improvement in quality and increase in disease resistance, the tilth and moisture relationships of the soil must be considered and adequate provision made through cultural practices to maintain the soil in good tilth and provide an adequate moisture-holding capacity so that growth may continue under adverse conditions. No tobacco plant is any better than its root system, and only in this manner may a normal root system be developed in unfavorable seasons.

Practices which provide such assurance of continued growth, adequate potassium uptake, and the quality and resistance which this guarantees, may be briefly summarized as follows:

The site must be selected with respect to good drainage. Good tilth must be provided. Humus must be supplied, preferably through the application of well-rotted animal manure, but if this is unavailable green manure may be substituted. It must be plowed under in the succulent state if a crop is to be planted at once. Rotations should be arranged so that the tobacco crop is never transplanted to a field in which old legume residues have just been plowed under. Cultivation should be adequate and should not damage or restrict root growth. Fertilizer applications should be sufficient to meet the demands of the crop and should include at least three times as much potash as nitrogen. The method of application should promote rather than restrict root development.

The experience of practical growers who have followed this system, and the results of experimental plot work, indicate that in this manner good yields of excellent quality tobacco, free from disease, may reasonably be expected in the face of climatic conditions that prove disastrous to the crop in general.



# POTASH IN RELATION TO CITRUS NUTRITION<sup>1</sup>

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During the past 35 years, many field trials with potash have been made in representative citrus orchards of California. In few, if any, cases have positive results of a decisive nature been obtained. Despite this fact, many growers persist in the belief that supplemental potash is essential for the maintenance of yields and for the production of quality fruit.

In a comprehensive survey of California citrus-orchard soils, wide variations in the total, exchangeable, and water-soluble potash content have been found. These results suggest that in some areas potash may be deficient; and that in others, through the consistent and long-continued use of manures and mixed fertilizers on soils initially rich in potash, injurious quantities of this element may have accumulated. In an effort to develop more reliable criteria for evaluating the potassium status of citrus-orchard soils, a comprehensive study of the potassium nutrition of citrus has been undertaken. The work, so far, has included three experiments: the first, a greenhouse experiment to determine the symptoms of potassium deficiency on several species of citrus grown in sand cultures under various nutritional conditions; the second, a solution-culture experiment with bearing citrus trees grown out of doors, to determine the effects of both potassium deficiency and excess on appearance of the tree, fruiting behavior, and fruit quality; and the third, an experiment to determine the reliability of tissue analysis as an index of the potassium status of the citrus tree. A full account of the first experiment and progress reports on the principal results, to date, of the other two studies are presented in this paper.

## EXPERIMENT 1—GREENHOUSE STUDY TO DETERMINE EFFECTS OF NUTRIENT VARIABLES ON SYMPTOMS OF POTASSIUM DEFICIENCY

The effects of potassium deficiency on citrus have not, heretofore, been thoroughly described, and the published information is somewhat conflicting (1, 2, 5, 8). It was thought advisable, therefore, to determine at the outset: (a) something of the range of potassium-deficiency symptoms on several species of citrus grown under various nutrient conditions; and (b) the extent to which potassium deficiency is delayed or accelerated by these and certain climatic variables.

### *Materials and methods*

Automatically operated sand-culture equipment was used for this experiment. Each culture unit consisted of a 135-liter tile reservoir, on top of which were set three 3-gallon glazed earthenware crocks filled with a sand-magnetite mixture

<sup>1</sup> Paper No. 476, University of California Citrus Experiment Station, Riverside, California.

flushed periodically with nutrient solution from the reservoir. The details of this type of equipment have been described elsewhere (3).

TABLE 1  
*Composition of nutrient solutions used in sand cultures\* in greenhouse*  
In amounts per liter†

NUTRIENT SOLUTION		CULTURE UNITS	CITRUS SPECIES TREATED	Ca	Mg	K	Na	Cl	NO <sub>3</sub>	SO <sub>4</sub>	PO <sub>4</sub> ‡
				m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.
Low-nitrogen	Complete	1 and 25	Sweet-orange seedlings Lemon cuttings, grapefruit seedlings	3.00	1.50	1.50	0.48	0.28	1.00	5.00	0.20
	-K	9 and 17 10 and 18§	Sweet-orange seedlings Lemon cuttings, grapefruit seedlings	4.00	2.00	0.00	0.48	0.28	1.00	5.00	0.20
Medium-nitrogen (Ca and Mg)	Complete	3 4§	Sweet-orange seedlings Lemon cuttings, grapefruit seedlings	5.00	2.50	2.50	0.48	0.28	5.00	5.00	0.20
	-K	11 12§	Sweet-orange seedlings Lemon cuttings, grapefruit seedlings	6.66	3.34	0.00	0.48	0.28	5.00	5.00	0.20
High-nitrogen (Ca and Mg)	Complete	5 and 29 6 and 30§	Sweet-orange seedlings Lemon cuttings, grapefruit seedlings	12.50	6.25	6.25	0.48	0.28	20.00	5.00	0.20
	-K	13 and 21 14 and 22§	Sweet-orange seedlings Lemon cuttings, grapefruit seedlings	16.66	8.34	0.00	0.48	0.28	20.00	5.00	0.20
High-nitrogen (Mg)	-K	7	Sweet-orange seedlings	5.00	20.00	0.00	0.48	0.28	20.00	5.00	0.20
High-nitrogen (Na)	-K	19 and 27 20 and 28§	Sweet-orange seedlings Lemon cuttings, grapefruit seedlings	4.00	2.00	0.00	19.48	0.28	20.00	5.00	0.20
High-sulfate (Ca and Mg)	-K	23 and 24	Sweet-orange seedlings	16.66	8.34	0.00	0.48	0.28	5.00	20.00	0.20
High-sulfate (Na)	-K	31 32§	Sweet-orange seedlings Lemon cuttings, grapefruit seedlings	4.00	2.00	0.00	19.48	0.28	5.00	20.00	0.20
High-chloride (Ca and Mg)	-K	15 16§	Sweet-orange seedlings Lemon cuttings, grapefruit seedlings	19.33	9.67	0.00	0.48	19.28	5.00	5.00	0.20
High-chloride (Na)	-K	8	Sweet-orange seedlings	6.66	3.34	0.00	19.48	19.28	5.00	5.00	0.20
High phosphate (Ca, Mg, and Na)	-K	26	Sweet-orange seedlings	6.66	3.34	0.00	3.48	0.28	5.00	5.00	3.20

\* Each culture unit consisted of a 135-liter tile reservoir containing the nutrient solution, and three 3-gallon glazed earthenware pots containing the sand-magnetite mixture and one citrus plant per plot. The pots were flushed with the nutrient solution once daily.

† Mn, B, and Zn were added at a rate of 1 p.p.m.; as a source of iron, 0.5 per cent magnetite was incorporated in the sand.

‡ The phosphate was later increased to 0.5 m.e.

§ Two of the three pots of each unit contained one lemon cutting each; the other pot contained a grapefruit seedling.

Potassium-deficient nutrient solutions varying widely in calcium, magnesium, sodium, nitrate, sulfate, phosphate, and chloride content were provided. A

number of units containing complete solutions of varying composition served as checks. The composition of the nutrient solutions is set forth in table 1. Manganese, boron, and zinc were added at the rate of 1 p.p.m. The sand contained a small amount of potassium, sufficient only to give the plants a good start. Finely ground magnetite, at the rate of 0.5 per cent, was incorporated in the sand as a source of iron.

In all save the low-nitrogen series of solutions, the nutrient level was high enough to provide ample amounts of all constituents. The aim with the low-nitrogen cultures was to produce plants slightly nitrogen-deficient. In devising these solutions, the thought was that any tendency of the citrus plant to absorb excessive amounts of other elements when potassium is deficient should be greatly intensified in cultures in which the concentrations of nitrogen, sulfate, chloride, phosphate, calcium, magnesium, and sodium, respectively, were increased; hence any symptom resulting from excessive accumulation of one or more of these ions should be accentuated.

Although no attempt was made to maintain unvarying concentrations of all ions in the various cultures, phosphate, pH, and nitrate were determined frequently, and appropriate adjustments were made. New solutions were prepared every two months. Water lost by transpiration and evaporation was compensated for by daily additions of distilled water. The sand cultures of each unit were thoroughly flushed once daily with nutrient solutions from the tile reservoir. The large volumes, frequent adjustments, and bimonthly renewals of the solutions, and the slow growth of the potassium-deficient plants prevented substantial changes in the concentration of the solutions.

The cultures were arranged in such a way as to facilitate comparisons, and duplicate cultures were so spaced in the greenhouse as to check on the effect of minor heat and light variations. Orange and grapefruit seedlings carefully selected for uniformity were transplanted from flats of soil into the sand. The lemon cuttings (Eureka) were rooted in sand in a propagating bed. Adhering soil and sand were thoroughly washed from the roots of all plants before transplanting into the pots. There were three plants per pot at the outset; later these were thinned to one plant per pot. The experiment was begun on October 20, 1938, and continued until October, 1939.

### *Results*

In a previous experiment, potassium deficiency was produced in a few sweet-orange seedlings, and symptoms were noted. The cultures of the present experiment were therefore watched closely for the appearance of the first symptoms characteristic of this disorder.

*Sodium accumulation.* The first symptom of malnutrition to appear in the potassium-deficient cultures was a burn on the older leaves of the plants receiving high  $\text{NaNO}_3$ . Subsequently, the plants receiving equivalent amounts of sodium from  $\text{Na}_2\text{SO}_4$  and  $\text{NaCl}$  showed a similar type of burn. Analysis of a sample of injured leaves showed 0.88 per cent sodium, on a dry-matter basis. Uninjured leaves of the same age showed 0.026 per cent sodium.

More or less burn of the older leaves of all the plants in the high-sodium cultures continued to occur throughout the experiment, though the plants receiving  $\text{NaNO}_3$  were affected more adversely than those supplied with  $\text{NaCl}$  or with  $\text{Na}_2\text{SO}_4$ . During hot spells the burn increased in amount. The injured leaves fell prematurely, but the total growth of the plants was not reduced much

TABLE 2

*Composition of orange leaves from seedlings grown in complete and in potassium-deficient nutrient solutions of variable composition*

Source, age, and character of leaves tested

NUTRIENT SOLUTION		CUL- TURE UNITS	AGE OF LEAF (AP- PROXI- MATE)	DESCRIPTION OF LEAF SAMPLE	CONSTITUENTS OF DRY MATTER, AT 105°C.									
					Ash	Ca	Mg	K	Na	N	P	S	Cl	
Low-nitrogen	Complete	1	months		per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	
			6	Yellow; nitrogen-defi- cient	14.00	2.43	0.11	3.45	0.03	1.42	0.12	0.33	0.14	
	12	Green, from stem base	17.00	4.24	0.20	2.70	0.05	1.49	0.12	0.50	0.15			
	-K	9	6	Medium yellow; crinkled	11.90	3.72	0.52	0.11	0.06	2.47	0.12	0.36	0.13	
12			Green, from stem base	22.30	6.75	0.65	0.06	0.13	2.05	0.12	0.69	0.11		
Medium-nitrogen (Ca and Mg)	Complete	3	12	Green, from base of plant	17.40	4.95	0.22	2.05	0.00	2.54	0.10	0.00	0.00	
	-K	11	6	Green; crinkled	15.20	4.97	0.63	0.15	0.00	3.26	0.08	0.00	0.00	
High-nitrogen (Ca and Mg)	Complete	5	12	Green, from stem base	22.15	7.14	0.66	0.23	0.00	2.43	0.15	0.00	0.00	
			6	Green	14.15	2.18	0.22	2.38	0.02	2.90	0.14	0.37	0.15	
	-K	13	6	Dull green; yellow spots; crinkled	17.32	4.22	0.23	2.94	0.01	2.59	0.14	0.30	0.12	
			12	Green, from stem base	15.35	5.20	0.59	0.13	0.01	3.18	0.10	0.29	0.13	
High-nitrogen (Mg)	-K	7	6	Dull green; crinkled	22.20	7.52	0.64	0.22	0.04	2.46	0.14	0.29	0.11	
High-nitrogen (Na)	-K	27	6	Dull green; crinkled	10.20	2.74	0.62	0.17	0.00	3.16	0.12	0.00	0.00	
High-nitrogen (Na)	-K	27	6	Green; crinkled	12.30	5.02	0.61	0.25	0.40	3.02	0.12	0.00	0.00	
High-sulfate (Ca and Mg)	-K	23	6	Dull green; crinkled	15.65	5.17	0.57	0.19	0.02	3.30	0.12	0.35	0.07	
High-chloride (Ca and Mg)	-K	15	6	Dull green; crinkled	16.55	5.90	0.87	0.20	0.01	3.66	0.15	0.00	0.40	
High-chloride (Na)	-K	8	6	Dull green; crinkled	13.60	4.35	0.55	0.16	0.15	3.30	0.11	0.00	0.34	
High-phosphate (Ca, Mg, and Na)	-K	26	6	Dull green; crinkled	17.35	5.84	0.80	0.16	0.00	3.22	0.20	0.00	0.00	

more than that of plants in other potassium-deficient cultures. Inasmuch as all the high-sodium cultures lacked potassium, it is not known to what extent the sodium burn was aggravated by potassium deficiency. However, results of leaf analyses, presented in tables 2 and 3, indicate a tendency toward sodium accumulation in the leaves of potassium-deficient plants; hence it is inferred that sodium injury is accentuated when potassium is lacking.

*Boron injury.* The next symptom to appear on the minus-potassium plants was a leaf mottling on the lemon cuttings, identical in appearance with that caused by boron excess. Analyses of such leaves for boron showed values ranging from 152 to 200 p.p.m., whereas leaves of comparable age from the control cultures showed only 20 to 40 p.p.m.

TABLE 3

*Composition of lemon leaves from cuttings grown in complete and in potassium-deficient nutrients of variable composition*

NUTRIENT SOLUTION		CULTURE UNITS	AGE OF LEAF (APPROXIMATE)	DESCRIPTION OF LEAF SAMPLE	CONSTITUENTS OF DRY MATTER, AT 105°C.								
					Ash	Ca	Mg	K	Na	N	P	S	Cl
			months		per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
Low-nitrogen	Complete	2	6	Yellowish; nitrogen-deficient	9.75	1.74	0.17	2.50	0.03	1.18	0.16	0.16	0.15
	-K	18	6	Yellowish; small leaves	11.90	3.98	0.34	0.05	0.16	2.22	0.11	0.35	0.11
Medium-nitrogen (Ca and Mg)	Complete	4	6	Green	11.65	2.90	0.27	1.61	0.00	2.06	0.12	0.00	0.00
			12	Green, from stem base	14.55	5.15	0.36	1.55	0.00	2.43	0.12	0.00	0.00
	-K	12	6	Yellowish; vein chlorosis; small leaves	12.30	3.90	0.43	0.13	0.00	2.90	0.12	0.00	0.00
			12	Green, from stem base	14.55	4.84	0.55	0.09	0.00	2.72	0.10	0.00	0.00
High-nitrogen (Ca and Mg)	Complete	6	6	Green; medium large	11.72	2.48	0.25	2.62	0.03	2.70	0.15	0.28	0.35
	-K	14	6	Greenish; some vein chlorosis; medium large	13.14	4.60	0.52	0.39	0.09	2.92	0.12	0.40	0.15
High-nitrogen (Na)	-K	20	6	Green; some Na burn; mild K-deficiency	11.72	3.32	0.32	0.23	0.63	3.17	0.12	0.00	0.00
High-sulfate (Ca and Mg)	-K	24	6	Yellowish; small leaves	13.05	4.36	0.45	0.18	0.00	3.60	0.13	0.44	0.00
High-sulfate (Na)	-K	32	6	Yellowish; small leaves; slight Na-burn	9.15	2.72	0.32	0.19	0.36	0.00	0.14	0.26	0.00
High-chloride (Ca and Mg)	-K	16	6	Yellowish; small leaves; vein chlorosis	10.67	3.66	0.35	0.14	0.00	2.62	0.14	0.00	0.29
			9	Bronzed; burned; gum spots	16.64	5.80	0.57	0.11	0.00	2.65	0.12	0.00	0.30

Curiously enough, the lemon cuttings receiving high concentrations of sodium, either as nitrate or as sulfate (cultures 20, 28, and 32), did not show symptoms of boron excess, though they were as much depressed in growth at this stage as the cultures showing symptoms of boron injury. Hence, the accumulation of boron in the potassium-deficient cultures was not wholly the result of retarded growth. Rather it appears that potassium and sodium influence boron absorption, potassium deficiency favoring boron accumulation, and sodium excess depressing it.

*Potassium-deficiency symptoms of orange and grapefruit seedlings.* Except for



the appearance of the aforementioned sodium burn and boron mottling of the leaves, the minus-potassium plants showed no other symptoms save retarded growth rate until April, 1939. At this time the leaves of the sweet-orange and grapefruit seedlings, in all except the high-sodium cultures, began to display a tendency to curl, pucker, and twist.

During the succeeding two months (May and June), these leaf abnormalities became much more pronounced. The curling and crinkling of the orange and grapefruit leaves were accompanied by a lusterless appearance and more or less fading of the chlorophyll. No distinctive or uniform leaf pattern developed, however. Some of the crinkled leaves retained their green color, others developed light-colored spots or areas irregular in size and spacing, and others showed a yellowing of a part of the veins. This last-named symptom was especially marked in the grapefruit, as was also the yellow spotting. At this time many of the older leaves showed the usual fading which accompanies senescence, the petiole in particular becoming yellow, the yellowing often extending to the lower part of the leaf blade. Many of the old orange leaves showed a dark discoloration on the upper leaf surface, especially around the margins. This was due to gum exudation and should not be confused with the marginal discoloration and burn prevalent on leaves of other potassium-deficient plants. In fact, marginal leaf scorch (4) was conspicuously absent in the citrus plants.

A month or more after the appearance of the puckered and crinkled condition of the leaves, the orange and grapefruit plants began to send out numerous lateral shoots. These shoots were spindly and weak, often drooping somewhat at a point near the main stem. In early stages the stem bark at this point was distinctly yellowish, but as the stem hardened, the bark turned green, and the direction of growth became more upright. This gave the shoots an S-shaped form. This secondary stage of potassium deficiency corresponds to that described by Nightingale (7) and by Wall (9).

Another condition that became pronounced on both the orange and the grapefruit plants was a gum exudation from split areas in the older stems and trunk.

The pronounced crinkling and curling of leaves, the weak, multiple lateral shoots, and an extreme case of the spotting and partial vein chlorosis of leaves are shown in figure 1.

*Potassium-deficiency symptoms of lemon cuttings.* The curling and puckering so prominent on the leaves of the orange and grapefruit seedlings was much less pronounced on the leaves of the lemon cuttings. The first tangible symptom to develop on the lemon cuttings was a distinct yellowing of the midrib of previously green leaves. This yellowing subsequently spread to some of the main veins and to adjacent mesophyll areas. At this stage the yellowed areas contrasted sharply with the green of the rest of the leaf. Later, as the whole leaf became more yellow, this symptom was less conspicuous.

Soon after the development of the veinal yellowing, many weak lateral shoots began to emerge, as in the case of the orange and grapefruit seedlings. Although laterals of the lemon cuttings did not show quite the drooping tendency of those of the orange and grapefruit seedlings, the stems were yellowish and, in areas, the bark became shriveled or pitted. In severe cases the shrunk or pitted



FIG. 1. EFFECTS OF POTASSIUM DEFICIENCY ON SWEET-ORANGE AND GRAPEFRUIT SEEDLINGS

A, Sweet-orange seedling showing crinkling and curling of leaves and weak, multiple lateral shoots; B, extreme case of leaf-spotting and partial vein chlorosis on grapefruit seedling.



FIG. 2. LEMON LEAVES SHOWING VARIOUS CONDITIONS CAUSED BY POTASSIUM DEFICIENCY

A, Early stages of potassium deficiency are characterized by a pronounced yellowing along midrib, which later spreads to veins and adjacent areas; B, old leaf showing small gum spots along veins; C, brownish gum spots along margin, and general irregular yellowing of leaf. Not all leaves showed all of these symptoms.

areas became necrotic and a dieback of shoot apices resulted. The leaves of shoots were small and underdeveloped.

Except for the early vein chlorosis, the lemon leaves showed no other charac-

teristic pattern. The leaves became unevenly faded and lusterless, and small gum spots often appeared along the main veins as the leaves aged. Small brownish spots also appeared along the margins of many leaves, and there was some tendency for yellowish and finally necrotic spots to develop. No marginal burn or scorch was evident at any time.

Lemon leaves showing various symptoms of potassium deficiency are presented in figure 2. The shrunken and pitted condition of the bark of a succulent young stem of a lemon cutting is shown in figure 3. No bark splitting or gumming was noted on the stems of the lemon cuttings.

*Effect of nutrient and climatic variables on potassium-deficiency symptoms.* Aside from the sodium burn and the symptoms of boron excess already mentioned, the character of the potassium-deficiency symptoms was essentially the same on all the plants, irrespective of the variations in the calcium, magnesium, sodium, nitrate, chloride, sulfate, and phosphate concentrations of the culture solutions.

The only difference noted was in cultures that were slightly deficient in nitrogen, where the secondary growth, characterized by the emergence of many weak laterals, was not so marked as in other cultures. This is in accord with the conclusions of Nightingale (7), that the secondary growth is a result of the accumulation of soluble organic nitrogen fractions. In plants partly nitrogen-starved, such accumulations would be less marked than in plants plentifully supplied with this element; hence it is to be expected that the amount of secondary growth in such plants would be reduced.

Another character somewhat transient in nature, not consistently seen, and unrelated to any of the nutrient variables, was that of iron chlorosis. That iron metabolism is somehow disturbed by potassium deficiency is seen in the nodal accumulations of iron in stalks of corn plants lacking potassium (6). The transient and inconsistent appearance of this symptom in citrus suggests that some climatic variable is involved.

On two occasions, during the late spring and summer (May and July) of 1939, potassium-deficient and corresponding control cultures of the low- and high-nitrogen series were stressed for water to see whether this would lead to any type of leaf burn or scorch. The nutrient solution with which the pots were customarily flushed once a day, was withheld for a sufficient period to induce incipient wilting. On neither occasion did burn or other leaf symptom develop. This result is in contrast to effects on other plants (4). It is a common observation that drought affects potassium-deficient plants more adversely because of a decrease or change in the water-retaining capacity of colloidal constituents.

As mentioned earlier, during hot spells the sodium burn always became more pronounced. In contrast, none of the potassium-deficiency symptoms were noticeably aggravated by high temperatures.

*Effect of potassium deficiency on mineral composition of plants.* To determine the effect of potassium deficiency on the mineral composition of the plants grown in the various nutrient media, leaf samples were picked from all cultures in October, 1939. The leaves were carefully cleaned, air-dried, and analyzed for mineral constituents. The results are shown in tables 2 and 3.



FIG. 3. ENLARGED SECTION OF YOUNG STEM OF A LEMON CUTTING, SHOWING SUNKEN OR PITTED AREAS OF BARK

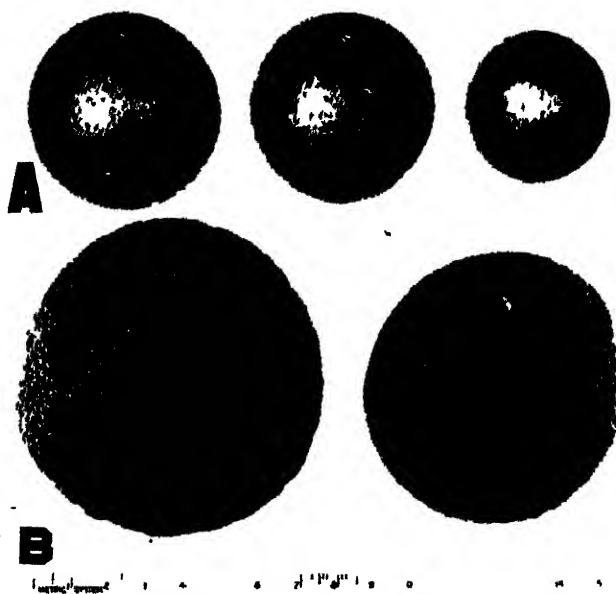


FIG. 4. EFFECT OF POTASSIUM DEFICIENCY AND EXCESS ON SIZE AND CHARACTER OF FRUIT PRODUCED

A, Fruit from potassium-deficient tree (no. 6), and B, from potassium-excess tree (no. 7)

As was to be expected, potassium was exceedingly low in all the potassium-deficient cultures. This deficiency was, in most cases, accompanied by an increase in accumulations of calcium and magnesium. The tendency toward calcium and magnesium accumulations appeared to be limited, however, as is shown by the fact that substantial increases of these elements in the nutrient solution were not accompanied by corresponding increases in the plant. In other words, though lack of potassium tends to cause increased calcium and magnesium absorption, there is some factor which operates to limit this absorption beyond a certain point.

There was a tendency for sodium to increase where potassium was lacking.

Lack of potassium resulted in increased nitrogen content of leaves in most cases; but, as with calcium and magnesium, this tendency was definitely limited. On the other hand, potassium deficiency did not result in significant increases of phosphorus, sulfur, or chloride in the leaves, though there was some increase in each of these elements where the nutrient level was markedly increased.

In general, the results of these analyses are in harmony with the finding that, so far as external symptoms of potassium deficiency are concerned, wide variations in calcium, magnesium, sulfate, chloride, and phosphate produced no detectable differences.

*Effect of nutrient variables upon severity of potassium-deficiency symptoms.* Unfortunately for this aspect of the problem, the plants made a somewhat uneven start, those receiving higher amounts of  $\text{Ca}(\text{NO}_3)_2$  in both the complete and the potassium-deficient cultures being somewhat depressed in the very early growth stages. Later this condition disappeared.

One fact became clear as the experiment progressed. The onset of potassium deficiency was significantly delayed by high concentrations of sodium. This was true of all three of the citrus species employed and in all seven of the cultures in which the sodium level was high. Though the older leaves on all of these plants showed sodium burn, the total growth was not materially depressed; hence the delay in the appearance of potassium-deficiency symptoms cannot be ascribed to slower early growth. Whereas all the other plants began to show signs of potassium deficiency in April, 1939, it was not until July, 1939, that the plants of the cultures high in sodium nitrate, sulfate, and chloride became affected. Subsequently, these plants developed exactly the same deficiency symptoms as all the others of this experiment.

The onset of potassium deficiency in culture 26 (high-phosphate), which received 3.48 m.e. per liter of sodium, was not delayed. These observations suggest that the effect noted in the high-sodium cultures was not due to partial replacement of the potassium function by sodium. Rather it appears that sodium offset the aggravating effects of calcium and magnesium. Despite the uneven start of these plants, there was evidence all through this experiment that increased concentrations of the divalent bases heightened the severity of the potassium-deficiency symptoms.

EXPERIMENT 2—EFFECTS OF POTASSIUM DEFICIENCY AND EXCESS ON BEARING ORANGE TREES GROWING IN SOLUTION CULTURES OUT OF DOORS

The study of the effects of potassium on bearing orange trees is still in progress, and, as final conclusions cannot yet be drawn, only a brief account of the technique and major results to date is given here. The experiment was set up to determine the effects of various potassium concentrations, including deficiency and excess levels, on the appearance, growth behavior, and quality of fruit produced. It was hoped, also, that the trees on this experiment would provide material for critically testing whether the potassium content of any part of the tree might serve as a reliable guide to potassium deficiency or excess.

The trees used (Valencias and navels on sour stock) were 5 years old from the bud and had been employed previously in a nitrogen experiment in outdoor sand cultures. They were transferred from the sand cultures to large, 700-liter, cylindrical, concrete containers in June, 1940.

The 20 trees of this experiment were divided into three groups: one group received potassium at a level ranging between 3 and 7 p.p.m.; another, between 30 and 40 p.p.m.; and the third, between 350 and 400 p.p.m.

Inasmuch as no evidence of potassium deficiency had developed in any of the low-potassium cultures by March, 1941, one tree was thenceforth deprived of this element. The only sign of malnutrition that appeared on this tree during the succeeding year was a reduced amount of new growth coupled with a greater fall of old leaves. This gave the tree a somewhat thinner appearance. The color of the foliage, especially on the sun side, was slightly less green. The tree set and matured a fair amount of fruit. The fruit was of good quality but somewhat small. During this period (March, 1941, to January, 1942) the potassium content of the leaves dropped from about 0.6 per cent to 0.2 per cent. There were no other distinctive symptoms, save a tendency toward slight iron chlorosis and symptoms of boron excess on a few leaves.

After the spring bloom, in April, 1942, defoliation became much more marked, the color of leaves became somewhat more bronzed, and in June, 1942, weak, S-shaped laterals, identical with those seen in the potassium-deficient greenhouse plants, began to emerge. Some of the older leaves began to show crinkling and twisting and the characteristic yellow spotting; others, on the south side of the trees, became severely sunburned. It is of interest that these distinctive symptoms did not appear until over a year after this tree had been deprived of potassium. This indicates that the early or incipient stages of potassium deficiency on bearing citrus trees cannot be diagnosed by external \*symptoms.

None of the trees maintained at from 3 to 8 p.p.m. potassium over a 2-year period have shown any signs of malnutrition. They are green, healthy, and vigorous, and, in every respect, normal in appearance.

The trees receiving 350 to 400 p.p.m. potassium have, however, developed marked symptoms of malnutrition. The earliest effects noted were on the fruit, many being large and misshapen. A great many of the fruits, particularly the

Valencias, had extremely coarse, thick rinds. The quality was poor, and the juice was low in total solids and acid. Leaf and fruit analyses showed a high-potassium and a low-calcium content.

Several of these high-potassium trees have become infected with brown rot gummosis, and during the first year, many of the fruits showed water spot and black rot.

The relative size and rind texture of typical fruit produced on trees suffering from potassium deficiency and excess, respectively, are shown in figure 4. As this experiment progresses, a more complete understanding of the growth and fruit abnormalities characterizing potassium variations should be obtained.

#### EXPERIMENT 3—FOLIAR DIAGNOSIS AS A MEANS OF DETERMINING THE POTASSIUM STATUS OF CITRUS TREES

Our studies to date indicate that neither for incipient potassium deficiency nor for incipient potassium excess are external symptoms sufficiently distinctive and specific for diagnostic purposes. Even in acute stages diagnosis from external symptoms alone is not too certain, because of possible complication by other, secondary factors. We have therefore begun a study to determine the reliability of tissue analysis as a diagnostic measure. Though this work is incomplete, encouraging results have been obtained.

For this disorder, the leaf appears to be the most indicative part of the tree. Forty to fifty leaves picked at random from an area approximately 3 to 7 feet high around the tree are sufficient to provide a representative sample.

Leaves from plants suffering from acute potassium deficiency are characterized by potassium contents ranging from 0.2 per cent to as little as 0.05 per cent, on a dry-weight basis. On the other hand, leaves from plants suffering from potassium excess may have as high as 5.0 per cent potassium in the dry matter.

As might be expected, the potassium content of leaves changes markedly with the seasons; it has therefore been necessary to standardize on leaves of known age. With oranges and grapefruit, the spring-cycle leaves which emerge with the bloom in April have been tentatively chosen for study. The potassium content of such leaves is at first comparatively high, but by July it has dropped to a level that remains fairly stable for several months. If the leaves are selected with care from fruit-bearing branches, one can be certain that they represent spring-cycle foliage.

On the basis of evidence thus far accumulated, it appears that spring-cycle leaves picked in July, August, or September and found to contain 0.2 per cent or less of potassium, indicate potassium deficiency. If the leaves contain over 1.0 per cent potassium and the tree is green and healthy, supplemental potassium is probably not needed. If the leaves contain 3.0 per cent potassium, or more, and are low in calcium content, a condition of potassium excess may be indicated. To date we have insufficient information to interpret leaf analyses showing values for potassium between 0.2 and 1.0 per cent. Moreover, the limits given as representing deficiency and excess levels are tentative, and further refinement and testing are needed before final standards can be established.

## SUMMARY

Greenhouse and outdoor experiments with citrus in controlled cultures have made it possible to determine some of the primary and secondary symptoms of potassium deficiency. Some of the effects of excess potassium on bearing trees have also been studied and described. The value of tissue analysis as an index of the potassium status of citrus trees has been partially investigated, the plants of these experiments and mature trees in the field being used for testing and for standardization of methods.

The early symptoms of potassium deficiency are reduced growth, sparse foliage, and a somewhat bronzed and lusterless appearance of the leaves, but at this stage there is nothing about the external symptoms to distinguish this disorder from many other conditions of malnutrition. Leaf analyses, however, show an abnormally low potassium content and increased percentages of calcium and magnesium. As the deficiency becomes more acute, there is evidence of leaf twisting and crinkling, and weak, spindly new lateral shoots emerge. Because of lack of mechanical strength, these shoots have, at first, a tendency to be S-shaped. No distinctive or uniform leaf pattern or patterns have been noted, though vein yellowing, yellow spots, markings, or stipplings are common. Conspicuous by their absence are the marginal discoloration and burn so commonly noted on the leaves of many other potassium-deficient plants.

Under greenhouse conditions the symptoms described above occurred on plants supplied with nutrients both low and high in calcium, magnesium, sodium, nitrate, sulfate, and chloride. This implies that these symptoms are primary and are associated with some fundamental disturbance of plant metabolism, caused by potassium deficiency. Potassium-deficient plants contained increased amounts of calcium, magnesium, sodium, and nitrogen, but the tendency for accumulation of these was not excessive. Phosphorus, sulfur, and chloride, on the other hand, did not accumulate in potassium-deficient plants.

Boron accumulated sufficiently in potassium-deficient lemon cuttings to produce on the leaves typical patterns of boron excess. Leaf burn from high sodium was somewhat accentuated by potassium deficiency. Transient iron-chlorosis patterns were frequently noted on the leaves. Stressing the greenhouse plants for water did not measurably aggravate the symptoms.

High concentrations of calcium and magnesium in the culture solutions slightly hastened the appearance of potassium deficiency; high concentrations of sodium delayed the onset of acute symptoms. Lower levels of sodium were without effect. It is suggested that the delaying effect of high sodium concentration was not due to its substitution for any function of potassium but rather to an antagonistic effect on calcium and magnesium, which tended to offset the aggravating effect of the divalent bases. Leaf analyses lend support to this view.

Fruit from potassium-deficient trees was smaller than that from healthy trees but was not of poor quality otherwise. Fruit from trees receiving excessive potash was large, coarse, more susceptible to rot, and of poor eating quality. The calcium content of such fruit was very low, and the symptoms noted may



have been the effect of calcium deficiency brought on by high potassium rather than any physiological effect of high potassium, as such, within the tree.

Studies of tissue analysis as a means of diagnosing potassium deficiency or excess indicate that under California conditions spring-cycle leaves picked in July, August, or September, from trees not affected by other types of malnutrition, are indicative of the potassium status of the tree. Further confirmation of these studies is necessary, but it now appears that leaves containing less than 0.2 per cent potassium probably indicate potassium deficiency; that those containing 1.0 per cent potassium, or more, indicate an ample supply of this element; and that those containing more than 3.0 per cent potassium and a subnormal amount of calcium may indicate potassium excess or calcium deficiency.

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# PLANT ANALYSIS AS A DIAGNOSTIC PROCEDURE

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The analysis of plants as a means of ascertaining the nutrient content of crops was undertaken early in the history of agricultural chemistry. De Saussure (17) in 1804 analyzed the ash of plants and observed that its composition varied with the soil, with the part of the plant, and with the age of the plant. Liebig (12, p. 203) and later Wolff (25) considered the maintenance of soil fertility similar to bookkeeping in which the nutrients removed by the crops must be restored to the soil either directly or indirectly. Hall (5) at Rothamsted in 1905 envisaged plant diagnosis as a determination of the "normal" nutrient content of the plant, but concluded that "... though the straw [of barley] shows very considerable fluctuations in its potash content it is not always possible to interpret the results." In 1928 Salter and Ames (16), after due consideration of the problem, concluded that so many factors influence the nutrient composition of the plant that the use of plant analysis as a guide for evaluating the fertilizer requirements of crops is precluded.

Notwithstanding the many difficulties, progress has been made in the use of plant analysis as an aid in diagnosing the nutrient requirements of plants. A significant step was taken by Hoffer (9) through the use of tissue tests for nitrates and potassium in the corn plant under field conditions. Later these "quick tests" were improved by Thornton *et al.* (21) and extended to include other nutrients. Further contributions have been made by many workers, including Emmert (3), Carolus (1), Hance (6), Hester (7), Page and Burkhart (15), and Scarseth (18).

Simultaneously with the development of the "quick tests," another group of workers; namely, Lagatu and Maume (11), and later, Thomas (20), Chapman (2), Nightingale (14), and Ulrich (22, 23), adopted primarily the more accurate laboratory procedures for ascertaining the nutrient content of the plant. The greater accuracy of the laboratory methods has permitted quantitative studies of the interrelationships of nutrients to yields, such as those presented by Lagatu and Maume (11) and Thomas (20). These workers have developed the concept of foliar diagnosis, which includes a study of the "course of nutrition" as reflected by its "intensity" (sum of percentages of N, K<sub>2</sub>O, and P<sub>2</sub>O<sub>5</sub>) and by its "quality" (ratio of N, K<sub>2</sub>O, and P<sub>2</sub>O<sub>5</sub>, calculated as milliequivalents and then expressed in per cent of the total milliequivalents). Their concept, however, has not been utilized by other workers. Rather, a simplified viewpoint has been

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adopted in the selection of critical levels or limits of each nutrient, which from previous experience have indicated deficiencies of a nutrient. The latter approach to the problem is common to the "quick tests" and to the laboratory procedures of other investigators, although the limits set by the "quick tests" are necessarily broader than for the laboratory methods.

#### CRITICAL CONCENTRATION OF A NUTRIENT

##### *Definition*

In the present paper the *critical nutrient concentration*<sup>2</sup> of a plant, or part of a plant, is defined as that narrow range of concentrations at which the growth rate or yield first begins to decrease in comparison to plants at a higher nutrient level. Above the critical range there is no diminution in the rate of growth or in yield caused by a lack of the given nutrient, but when the concentration decreases to the critical level, or below it, the growth rate as well as the yield decreases. This definition is in accord with the one recently proposed by Macy (13).

##### *Determination*

Under conditions of known nutrient or fertilizer response, the critical level for each nutrient may be determined by sampling the proper part of the plant at regular intervals during the growing season. From the changes taking place in the nutrient concentration of the fertilized and unfertilized plants, the approximate critical range may be ascertained. In a field experiment with grapes, to be discussed later, the critical range is in the region of little change in the potassium concentration of the leaf petioles from the plots without added potassium (fig. 1). When similar low values are obtained at other localities, then a deficiency of that nutrient may be suspected and later tested by actual trial. Through many observations of this nature, in which responses are compared to analytical values, the critical concentration for each nutrient and for each crop may be established.

When it is possible to make frequent harvests of a crop during its development to maturity, a modification of the foregoing procedure may be employed for the determination of the critical range. Plants growing either in pots of soil or in nutrient solutions are supplied with two different amounts of the limiting nutrient, while all other growth factors are adequately maintained. At first there will be no significant difference in yield between the two series of plants, but later the yield of the plants with the smaller amount of the limiting nutrient will be less than the yield with the higher amount. The concentration of the limiting nutrient in a suitable part of the plant at the time of decreased growth will be its critical concentration. As in the first method of determining the critical concentration, additional experience in the field will aid in making general interpretations by this method.

<sup>2</sup> In a recent paper by the author (22) the "critical value" was designated as the "minimum value." The two terms, as used in this and in the former paper, are synonymous. At this time it appears preferable to reserve the term "minimum value" to designate the lowest concentration of a nutrient attainable in the plant or in any part of the plant.

Another and simpler method of determining the approximate critical nutrient range is through an analysis of parts of the plant, when the plant displays known nutrient deficiencies. Critical values estimated in this manner, as well as by the pot or the solution culture technique, are likely to be lower than the values obtained under field conditions.

TABLE 1

*Effects of stage of development, of season, and of sodium and calcium on potassium concentration of tomato leaf blades visibly deficient in potassium*

HARVEST DATES	TREATMENTS*	POTASSIUM IN DRY LEAF BLADES				
		1	2	3	4	Mean
		<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
February 5, 1941.....	Control	0.70	0.55	0.61	....	0.62
	Control + Na	0.79	0.95	0.90	....	0.88
February 19, 1941.....	Control	0.62	0.60	0.57	....	0.60
	Control + Na	0.65	0.63	0.75	....	0.67
March 5, 1941.....	Control	0.33	0.48	0.40	....	0.40
	Control + Na	0.54	0.51	0.48	....	0.51
Significant difference†.....		....	....	....	....	0.11
May 6, 1942.....	Control	0.53	0.48	0.56	0.58	0.54
	Low Ca	0.49	0.59	0.53	0.52	0.53
May 20, 1942.....	Control	0.34	0.48	0.34	0.43	0.40
	Low Ca	0.41	0.38	0.38	0.46	0.41
June 3, 1942.....	Control	0.42	0.42	0.34	0.39	0.39
	Low Ca	0.55	0.60	0.55	0.52	0.54
June 17, 1942.....	Control	0.35	0.30	0.32	0.32	0.32
	Low Ca	0.46	0.54	0.58	0.49	0.52
Significant difference†.....		....	....	....	....	0.07

\* Culture solutions for plants without sodium were the same as given in the text; those with sodium had an initial  $\text{Na}_2\text{SO}_4$  concentration of 0.005 *M*. The low-calcium plants were grown in solutions containing one quarter of the amount of calcium in the control solution. The nitrogen of the low-calcium solution was made comparable to the control solution with  $\text{NH}_4\text{NO}_3$ . The solutions in the control experiments were identical.

† At the 5 per cent level (4, 19).

### *Constancy of critical concentration*

Since the burden of the interpretation of plant analysis rests primarily upon the value of the critical nutrient concentration, the approximate constancy of this concentration is of the utmost importance. Undoubtedly some of the factors known to influence the nutrient content of the plant, such as soil, climate, and stage of development of the plant, will also affect the critical concentration of the

nutrient. Fortunately, the variations observed in the potassium concentration of plants grown in nutrient solutions, in pots of soil, and in the field have not been great. In two series of experiments with Marglobe tomatoes grown in aerated culture solutions,<sup>3</sup> studies were made of the effects of some of the foregoing factors upon the potassium concentrations of leaf blades that displayed potassium-deficiency symptoms. The results given in table 1 indicate that the potassium concentrations in each series of plants decreased as the deficiency increased in severity. Superimposed upon these effects were the influences of season. In February the average value was 0.61 per cent as compared to 0.47 and 0.36 per cent for May and June respectively. Sodium added to the culture solutions increased the potassium concentration of deficient blades for the March 5, 1941 harvest by 0.11 per cent. Potassium-deficient blades from culture solutions low in calcium were higher in potassium for the last two harvests than the blades from the control plants.

The general conclusion that may be drawn from these observations is, that even though the potassium concentrations of the deficient blades are influenced by sodium or calcium or by the season, the effects are not large enough to alter the interpretation of the values under field conditions. Until additional experiments prove otherwise, therefore, the critical concentrations for potassium may be used as points of reference to ascertain the potassium status of the crop.

#### GENERALIZED PLANT NUTRIENT EQUATION

One of the criticisms of plant analysis as a diagnostic procedure has been that an interpretation of the analytical results is prevented by the many factors that influence the nutrient composition of the plant. It is this sensitivity of the plant to environmental changes, however, along with the narrow range of the critical nutrient concentrations, that makes plant analysis of value as an aid in determining the fertilizer requirements of crops. If plants were not influenced by their surroundings, plant analysis would have little value.

The many factors or variables affecting the nutrient concentration of the plant may be equated as Jenny (10) has done recently for the factors affecting soil formation. In an equation for plant nutrients, the concentration of a given nutrient ( $X$ ) would be a function of the soil ( $S$ ), climate ( $Cl$ ), time ( $T$ ), plant ( $P$ ), management ( $M$ ), and possibly others. This relationship may be expressed in the following generalized equation:

$$X = f(S, Cl, T, P, M, \dots)$$

Under field conditions specific values cannot be substituted readily in the foregoing equation, but nevertheless, a certain biological integration of these interrelationships is reflected at any one time in the analysis of the plant as a whole or of any part of it. The analytical value found, when compared to the previously established range of critical nutrient concentrations, permits a conclusion to be drawn concerning the nutrient status of the plant. When the con-

<sup>3</sup> The technique used in these studies was similar to that described in the section on the procedure of plant analysis.

centration of a nutrient is above the critical range, the supply of the nutrient is considered ample at the time of sampling, but when the nutrient concentration is at or below the critical range, the supply is inadequate.

From an inspection of the plant nutrient equation it will be seen that an analysis of the plant gives an integrated value of all the factors that have influenced its nutrient content up to the time of sampling. The quantity of a nutrient in the plant at any one time depends not only on the supplying power of the soil for the nutrient and on the total mass of soil accessible to the root system, but also on the factors that influence the growth of the plant. The faster a plant grows the greater will be its nutrient requirement (yield  $\times$  critical concentration). The extent and type of root development will again modify the relationships of nutrient supply to growth, and when all these factors are coupled with soil heterogeneity, the situation becomes extremely complex. No simple soil analysis can predict the outcome of all these interrelationships, but in contrast, an analysis of the plant in conjunction with a comparison to the critical nutrient range permits conclusions regarding the nutrient level in the soil.

#### PROCEDURE OF PLANT ANALYSIS

Since much of the experimental technique discussed in this paper is illustrated by data from fertilizer experiments with grapes and from an experiment with Marglobe tomatoes grown in culture solution, these will be described briefly.

In the field experiments with grapes one series of plots was in northern California, in Alexander Valley, near Healdsburg, on Corning gravelly loam; the other experiment was in southern California, at Guasti, on Tujunga sand. At Alexander Valley the plots of Petite Sirah grapes (on Rupestris St. George rootstock) were two rows wide and twenty vines long. The plots were separated by a single guard row. Each treatment (fig. 1) was replicated three times in a systematic manner so that a given treatment occurred but once in a block or tier. At Guasti, the plots of Mataro grapes consisted of two rows of twenty-seven vines each and were separated from adjacent plots by two guard rows. Each fertilizer treatment (table 2) was replicated six times so that it occurred at random but once in a block. At both locations the untreated soils had approximately the same potassium concentration, as determined by the Neubauer and replaceable methods. In all cases the fertilizers were applied to the plots in the bottom of plow furrows during January, and the subsequent rainfall was considered ample to make the fertilizers effective during the same year.

The Marglobe tomato plants were grown in aerated culture solutions (8) by the following technique: Twelve plants germinated in potassium-free sand were transferred at the two-leaf stage to 40-liter tanks. Each tank contained a culture solution of the following initial composition: 0.005 *M*  $\text{Ca}(\text{NO}_3)_2$ , 0.002 *M*  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ , 0.0025 *M*  $\text{NH}_4\text{NO}_3$ , 0.006 *M*  $\text{KH}_2\text{PO}_4$ , 0.002 *M*  $\text{MgSO}_4$ , 2.0 p.p.m. B, 2.0 p.p.m. Mn, 0.2 p.p.m. Zn, 0.08 p.p.m. Cu, and 0.02 p.p.m. Mo. In addition to the foregoing salts 1 ml. of 0.5 per cent ferric tartrate per liter of culture solution was added as required. The pH values of the solutions were adjusted to 4.5 to 6.5 with  $\text{H}_2\text{SO}_4$  when they became higher than 6.5.

Plants for each harvest were divided into three parts; namely, the upper, middle, and lower thirds. The middle thirds of the plants were separated into blades, rachises plus petioles, and stems. The blades and rachises after separation were placed into two groups; those with and those without visible potassium-deficiency symptoms. Plant material that was not separated was classified as residue. The roots were centrifuged to remove excess moisture and then dried. All material after being dried was weighed and then ground to pass a 40-mesh sieve.

### *Frequency of sampling*

The number of samples to be collected during the growing season will depend largely upon whether the study is to be intensive or extensive. In an intensive study it is necessary to take a number of plant tissue samples throughout the season in order to follow the nutritional trends taking place in a crop (11, 20). When surveying large areas for nutritional deficiencies, one sampling at a suitable time may suffice.

In the preliminary studies with grapes in the Alexander Valley (fig. 1) four samples were collected at intervals, starting at approximately blossoming time and continuing through to harvest. With frequent sampling it was possible to follow closely the changes in potassium concentration in the leaves. In the plots without added potassium the potassium concentration of the leaf petioles decreased rapidly to low levels by midsummer and then continued to decrease slowly to harvest time. The grape yields from these plots (3.14 tons per acre) were significantly less than those from plots fertilized with potassium (3.82 tons per acre), and therefore, these potassium concentrations were considered to be critical for grape production.

An inspection of the curves for potassium (fig. 1) indicates that midsummer would be a favorable period to take a single sample in order to conduct a survey of the potassium status of grape vines over a large area. Areas found to be low in potassium could be subjected either to further experimentation, or when sufficient information had been obtained, to fertilization with potassium. For some crops under some conditions the deficiency is subject to correction within a short time, as was accomplished by Nightingale (14) in his nitrogen applications to pineapple plants in the Hawaiian Islands. With perennials, the knowledge gained one season cannot be employed until the following year, and the changes in plant nutrient concentration and in yields caused by the fertilizer treatment may be observed much later. When the fertilizers do become effective, however, their influence may be observed years later, as at Alexander Valley where potassium applications made in 1935 through 1938 were still effective in 1941 in increasing both the potassium concentrations of the petioles and the yields.

### *Selection of plant part*

The part of the plant selected for analysis should reflect the general status of the plant with respect to the nutrient under consideration. In order to accomplish this objective effectively, the part selected must be of a definite

physiological age (11, 20), i.e., taken from a definite position on the plant, and furthermore, it should be as uniform as possible, for example, leaf petioles should be separated from blades, and stems from leaves.

In the Alexander Valley plots the importance of separating petioles from blades is indicated by a comparison of the changes in potassium concentration for the petioles (fig. 1) with those of the corresponding blades (fig. 2). This comparison shows that the range of potassium concentrations, as well as the differences in the

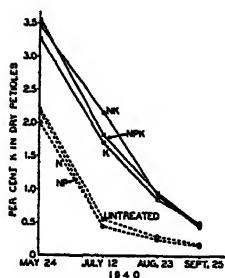


FIG. 1

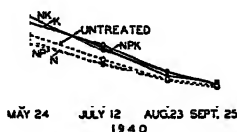


FIG. 2

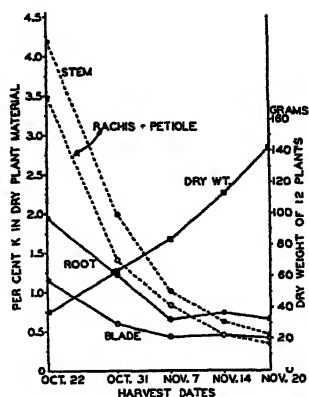


FIG. 3

FIG. 1. POTASSIUM CONTENT OF PETIOLES OF THE FIRST "MATURE" APICAL LEAVES TAKEN FROM THE FERTILIZER PLOTS OF PETITE SIRAH GRAPES IN ALEXANDER VALLEY, CALIFORNIA, IN 1940

N =  $\frac{1}{2}$  pound of  $(\text{NH}_4)_2\text{SO}_4$ ; P =  $\frac{1}{2}$  pound treble superphosphate; K = 1 pound  $\text{K}_2\text{SO}_4$  per vine applied each year from 1935 through 1938.

The grape yields in tons per acre for 1940 and 1941 were as follows: untreated, 3.10, 2.92; N, 3.31, 3.18; K, 3.87, 3.98; NK, 3.76, 3.66; NP, 3.01, 3.29; NPK, 3.83, 4.02. The effect of potassium on the yields of the K plots represents increases of 25 and 36 per cent over the untreated plots in 1940 and 1941 respectively.

FIG. 2. POTASSIUM CONTENT OF BLADES OF THE FIRST "MATURE" APICAL LEAVES TAKEN FROM THE FERTILIZER PLOTS OF PETITE SIRAH GRAPES IN ALEXANDER VALLEY, CALIFORNIA, IN 1940 SEASON

Fertilizer treatments and yields as in figure 1

FIG. 3. INFLUENCE OF TIME OF HARVEST ON DRY WEIGHT AND ON THE POTASSIUM CONCENTRATION OF LEAF BLADES, PETIOLES PLUS RACHISES, STEMS, AND ROOTS OF TOMATO PLANTS

potassium concentrations caused by the treatments, is much greater for the petioles than for the blades. On July 12 the potassium concentration of the petioles of the potassium-treated vines was on the average 4.04 times as great as that in the petioles of the untreated vines, whereas for the blades the corresponding figure was 1.34. This difference in sensitivity of the petioles to potassium changes is an obvious advantage in ascertaining the potassium status of grapes.

It might be assumed from the foregoing observations that the petioles of all kinds of plants would be preferable to the blades, but this was found not to be



true for tomatoes. In the experiment with Marglobe tomatoes grown in a culture solution low in potassium, plants were harvested at weekly intervals. At the time of the first harvest, on October 22, no potassium-deficiency symptoms were visible, but a week later the first incipient symptoms were noted, and thereafter the symptoms became more pronounced with each harvest. The potassium concentrations of the blades, rachises plus petioles, stems, and roots for each harvest date are given in figure 3. The rachises plus petioles of these plants, as in the grapes, had a greater potassium range than the blades, but the blades indicated the impending potassium deficiency earlier than an analysis of the other parts of the plant. This is a point of considerable practical importance in utilizing the data under field conditions.

For other nutrients the most favorable part of the plant for analysis must be ascertained. Recently the petioles of the most recently "matured" leaves of grapes (23) and of sugar beets (24) have been shown to indicate satisfactorily by their nitrate content the nitrogen status of these plants.

#### *Form of combination of nutrient in the plant*

The form of combination of the nutrient determined analytically offers no problem for potassium, since only total potassium is estimated, but for nitrogen and phosphorus, it is desirable to differentiate between the combined forms of these elements. The nitrate concentration of leaf petioles of grapes (23) and of sugar beets (24) has been found, for example, to indicate the nitrogen status of these plants better than a determination of the total nitrogen or total soluble or insoluble nitrogen. Moreover, unpublished data indicate that the phosphates extracted by 2 per cent acetic acid from Ladino clover petioles show the phosphorus status of the plant better than a determination of the total phosphorus.

#### *Relation of stage of growth to evaluation of data*

Generally, the earlier in the growing season a nutrient deficiency occurs, and the longer it lasts, the greater is the likelihood of a significant fertilizer response. In the experiment with grapes in Alexander Valley the potassium concentrations of the leaf petioles attained a low level in midsummer (fig. 1), whereas at Guasti the potassium concentrations did not reach a deficiency level until harvest time (table 2) (22). Vines showing an early deficiency responded to potassium whereas those showing a deficiency later in the season did not.

The difference in potassium response at Alexander Valley and at Guasti sets forth an interesting comparison of plant analyses and soil analyses. Since the replaceable and Neubauer potassium concentrations of the soil at the two locations were similar, the vines at both places should have responded similarly to potassium application. Experiments showed, however, that the responses were different. In contrast to the soil analyses, the plant analyses indicated correctly the potassium status of the vines at the two locations.

#### *Nutrient concentration and yields*

Yields do not continue to increase indefinitely with increasing nutrient concentration in the plant, but do so only when the nutrient concentration is in the

deficiency range. In this range an increase in the concentration of the nutrient will result in an increase in yield in comparison with the yield of plants with a lower nutrient concentration. When the concentration of a nutrient is above the critical range, then one of the many factors given in the plant nutrient equation would limit growth, and accordingly, no correlation between the nutrient concentration and the yields should be expected. Absorption of luxury amounts of a nutrient would disturb still more the correlations between yields and nutrient concentrations in the plant, when the latter are above the critical range.

TABLE 2

*Potassium concentration of leaf petioles contrasted with grape yields in 1941 from Mataro vines on Tujunga sand at Guasti, California*

TREATMENTS*	K IN PETIOLES			YIELD PER ACRE
	May 28	July 11	Sept. 20	Sept. 21
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>tons</i>
Untreated.....	2.73	1.49	0.37	2.83
N.....	3.24	1.67	0.44	3.89
P.....	2.53	1.41	0.37	2.59
NP.....	3.10	1.65	0.47	3.80
K.....	2.80	1.56	0.47	2.57
NK.....	3.09	1.75	0.54	3.57
NPK.....	3.03	1.80	0.54	3.72
Significant difference at the 5 per cent point.....	0.78	0.17	0.09	0.75

\* N = 1 pound  $(\text{NH}_4)_2\text{SO}_4$ ; P =  $\frac{1}{2}$  pound treble superphosphate; K = 1 pound  $\text{K}_2\text{SO}_4$  per vine applied each year from 1939 through 1941.

### *Sampling technique*

The procedure adopted for collecting plant samples from a field will modify the estimate of a critical level set for the crop. If samples are taken only from a few plants, or from plants with a visible nutrient deficiency, the appraised concentration of the deficient nutrient will be lower than when plants are collected from a large area. The larger the area from which the plant sample is taken, the greater is the likelihood of collecting material representing an average stage of deficiency. In a field with 50 per cent of the plants at the deficiency level, the remaining plants may increase the nutrient concentration of the composite sample above the critical range. Under these conditions it may be necessary either to take more samples over smaller areas or to raise the value considered as critical when employed as a basis to indicate a field that would respond as a whole to the application of the deficient element.

### *Nutrient balance*

An important consideration in the successful production of crops of high quality is an understanding of the nutrient balance within the plant. It may not

suffice to have each nutrient above the critical level, but in addition it may be necessary to have definite relationships between the nutrients and the products synthesized by the plant. These relationships will vary with climate and with the part of the plant harvested. When crops are harvested for their fruit, the balance of carbohydrates and nitrogen may be of especial importance, as Nightingale (14) has recently demonstrated with nitrogen for the pineapple plant. For some crops a high phosphate or potassium level may be necessary during or prior to the formation of fruit, or during certain periods of vegetative growth. These higher levels of nutrition may be essential to high quality.

### *Practical applications of plant analysis*

Some of the interesting uses to which plant tissue analysis may be put are in locating field fertilizer experiments efficiently and in suggesting fertilizer practices. Large areas may be surveyed intensively at low cost during the most critical period in the growth of crops. Areas found to be low in potassium, for example, could either be sampled more carefully or be used immediately as locations for fertilizer experiments in order to ascertain the responses made by the crop to the application of potassium to the soil. In this way, only the most likely areas would be subjected to the much more expensive and time-consuming procedure of field experimentation. After the responses to fertilizers have been demonstrated in the field, plant analysis alone may serve as an aid to making fertilizer recommendations for crops.

### SUMMARY

The concentration of a nutrient in the plant as a whole or in any part of it is a function of soil, climate, plant, time, management, and possibly other factors.

At any one time a chemical analysis of the plant or part of the plant gives an integrated value of all the factors that have influenced its nutrient composition. By comparing the nutrient changes taking place during the development of the crop with previously established critical levels, the nutrient status of the plant may be ascertained. Plants with nutrient concentrations above the critical values may be considered adequately supplied at that moment, whereas plants with values within the critical range may be considered inadequately supplied. The longer a deficiency persists, and the earlier during the growth cycle it occurs, the greater is the likelihood of a response upon the application of the deficient nutrient.

An inspection of the plant nutrient equation indicates that the supplying power of the soil for a nutrient is just one of the many factors affecting the concentration of nutrients in the plant. This accounts for the frequent failure of soil analysis to serve as a satisfactory guide for fertilizer practices.

The practical application of plant analysis as a diagnostic procedure rests essentially upon the reliability of the critical nutrient levels. The limited variations found in the critical potassium concentrations of appropriate plant tissues give hope that useful interpretations may be made.

The sensitivity of plant tests depends upon the part of the plant analyzed, the particular fraction of the nutrient determined (e.g., nitrate or organic nitrogen, inorganic or organic phosphorus) and the position on the plant from which the sample is selected.

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# PLANT-TISSUE TESTING IN DIAGNOSIS OF THE NUTRITIONAL STATUS OF GROWING PLANTS<sup>1</sup>

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Many fertilizer experiments have been handicapped or have failed to give true information because experimenters assumed that the growing crop was adequately supplied with a particular nutrient element. This assumption was strengthened if the nutrient had been added to the soil as a fertilizer in amounts assumed to be adequate. Mere addition to the soil is no assurance, however, that the nutrient is effectively entering the plant. Since only the nutrient that enters the plant is effective in feeding the crop, it is most important to know whether or not the plant is absorbing the nutrient. The failure of the plant to obtain the nutrient may depend upon many factors, such as too high placement of the fertilizer for the roots in drought periods, movement of the nutrient to the surface out of reach of the roots, leaching, fixation, poor root development or deficient aeration, and toxic root zones.

Many fertilizer experiments conducted to determine the crop response to a particular nutrient element have resulted in no increase in yield even though it was reasonable to believe that the soil was deficient in this element. In such experiments the effects of the other nutrient elements have presumably been eliminated by their addition as constants or by the thought that they were adequate in the soil. Since no response was obtained from the particular element being studied, the conclusion has unfortunately often been drawn that the element was not needed. It is in such instances that some information on the nutritional status inside the growing plant becomes most helpful.

## PURDUE PLANT-TISSUE TEST METHOD

It is possible to determine, with the Purdue plant-tissue test method (2, 4, 8), the nutritional status of a crop with respect to nitrate, inorganic phosphate, and potassium at any stage of growth. This technique has certain practical advantages and has served as a valuable diagnostic aid in evaluating the various soil treatments in the current fertilizer experiments in Indiana. Modifications in experimental work to eliminate some fundamental faults are being made as a result of information obtained with this procedure. The details of making the tests and the chemical solutions used have been described by Thornton, Connor, and Fraser (8). The use of this test in determining fertilizer needs has been described further by Scarseth (4).

The value of the Purdue tissue test as a diagnostic aid depends on the common

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sense of the operator in making a logical interpretation of the results. *He is compelled to abandon preconceived notions and must accept the facts presented by unalterable chemical reactions.* The following analogy may help to make clearer the concept the operator must have to interpret the results from the tissue tests:

If a machine in a factory is to operate at its full capacity, all the conveyors bringing in the raw materials must be running full. The supply of these materials in the stock piles must be adequate to keep each conveyor filled. Whenever a particular conveyor starts to run thin, it means that the supply in the stock pile of that material is low and the production of the machine must slow down to the rate of the intake of the element present in the least amount. The slow-down in production is the first response to a scanty supply of any of the necessary raw materials, because the quality of the finished product must be upheld to a certain standard. If, however, operations must proceed on a very deficient supply of a particular material, there is grave danger that the quality must also be sacrificed along with the reduced production.

A factory superintendent will keep an alert eye on the conveyors to see that they are always running full. He notes that when the rate of production slows down as a result of a scanty supply of material on one of the conveyors, the other raw materials tend to accumulate in unused forms on their conveyors in front of the machine. He is not fooled into thinking such a situation represents an over-supply of these materials in the stock piles.

This analogy becomes a reality when certain words are substituted. The cells in the plant become the machine where the manufacturing takes place; the nitrates, phosphates, potassium, and other nutrient ions are the raw materials; and the conducting tissues (xylem tubes) become the conveyors.

In making a rapid chemical determination of the contents of the plant tissues with the Purdue plant-tissue test method, the operator is, in fact, looking at the conveyors in the plant to observe whether plenty of such essential nutrients as nitrates, inorganic phosphates, and potassium are entering the plant and passing on to the points needed. This test indicates the presence or absence of these nutrients in the conducting tissues of the plant in soluble, *unassimilated* form.

When the intent is to ascertain the first limiting nutrient growth factor it seems important to differentiate between nutrients that have been assimilated and those that are unassimilated and still in the role of a raw material.<sup>2</sup>

It is for this reason the conveyor-tissue parts are cut instead of crushed or ground. The test does not show nutrients that have been assimilated into organic compounds. In these respects the Purdue method differs markedly from tissue tests in which the material is ground and emulsified, as in the Hester method (1); or in which analyses are made of the total contents of the nutrients in a part of the plant, as in Thomas and Mack's foliar diagnosis method (5, 6, 7); or in which small amounts of ash are analyzed by the spectrographic method of Lundegardh (3).

<sup>2</sup> The "assimilation" of potassium is not understood. A freshly cut plant that shows no potassium present by the tissue test method but contains potassium as shown by ash analysis may show a "high" test by the tissue test method after the plant is dried. Potassium will leach out of dried hay, but not out of the hay before it is dried. This indicates that the potassium is held by some form of adsorption in the living protoplasm.

## OBJECTIVES OF DIFFERENT PLANT-TISSUE TESTS

The Hester plant-tissue test is a relatively rapid laboratory method and has an important advantage in being quantitative. In the foliar diagnosis method of Thomas or in the spectrographic method, a quantitative laboratory analysis is involved. These methods are relatively long but invaluable in precision research. In the practical diagnosis of nutritional problems with growing crops, however, the semiquantitative results obtained with the Purdue method are most helpful because of the rapidity and ease of testing.

## NECESSITY FOR DIAGNOSTIC POINT OF VIEW

Whenever a crop falls below its optimum, the question arises: What is the factor or factors holding back performance? The diagnostician will examine all possible causes of trouble. How acid is the soil? Is it too acid for the crop or for legume bacteria? Is the acidity great enough to cause toxic amounts of soluble aluminum? Is the aeration so poor that it causes anerobic decomposition and the formation of toxic ferrous iron or  $H_2S$ , or the loss of nitrogen by denitrification? Has the soil a cropping history of depletion, or has manure, crop residues, or fertilizers been used? If so, to what extent and what kinds? How much corn, wheat, potatoes, soybeans, cotton, sugar beets, or other crops did the soil produce in past years? Do these yields reflect a high or a low state of fertility? What are the characteristics of the soil? Is it so low in organic matter that nitrogen may be one of the first limiting factors? Is it so dark colored or mucklike that  $K_2O$  may be the first limiting factor? The diagnostician may test the soil for so-called available nutrients. These tests, he recognizes, have limitations, but they add information.

On growing crops, the diagnostician looks for nutrient-deficiency symptoms. These are another guide, but they are not always conclusive, because internal nutrient situations may change as the plants develop or as the rainfall varies. He then goes a step further and analyzes the plants. A quantitative test of the tissues is desired in some instances, but in the practical diagnostic approach, the semiquantitative test is adequate, because the question is whether there is an abundance or an absence of soluble nutrients in the plant conveyors at the time of testing.

The tissue test will indicate a nutrient deficiency before the plants show the starvation symptoms.

Since the plant is a dynamic system growing out of an equally dynamic soil, where conditions of nutrition vary within the plant with the stage of growth, root development, and formation of the seed or fruiting body, and within the soil with moisture, fertilizer placement, aeration (oxidation and reduction), organic content (energy for microorganisms), temperature, and other factors, it is easy to see that variations in the soluble nutrients in a plant as it grows are to be expected. This complexity of conditions has discouraged some from attempting to make tissue tests. Nevertheless, if the nutritional status within the plant is determined frequently during the growing period, one gathers the



information regarding the factors of nutrition that are limiting at any particular period.

It has been said, "Here is a field that reflects low nitrate in one plant, low phosphate in another, and perhaps low potash in still another; therefore the tests are no good." In such a case the true situation is that the field is very deficient in all three nutrients, and the variations in tissue-test results are reflecting the true variation in the soil and in the plants. *It must be realized that the tissue test indicates only what element is the first limiting nutrient growth factor at the time of the test.*

A plant physiologist realizes that a plant is not uniform throughout its tissues in nitrates, phosphates, and potassium. On what tissue, therefore, should the best be made?

A plant so abundantly supplied with nutrients that more nutrients would not affect growth, would show a "high" test in any of its tissues.

As the supply of nutrients falls off, the lower part of the plant will become deficient in phosphate and potassium before the growing tissues in the upper part of the plant are deficient. Such a plant may be producing an acceptable yield, but this will not be so high as it would be if all parts of the plant gave a high test throughout the growing period. This occurs without exception on fields of high-yielding corn.

As the supply of nitrates decreases, the upper part of the plant, where maximum utilization is in progress, will show a low test for nitrates first. Nitrates may show "high" in the base of the plant stalk after the upper plant parts show "low." Such a plant may be growing acceptably well and show no nitrogen-starvation symptoms, but may be slightly handicapped in its growth because of a slight shortage. If the base of the stalk shows no nitrates, the plant is starving for nitrogen. The base of the stalk may show the presence of nitrates in the early morning but none later in the day when nitrogen metabolism has caused the plant to use the nitrates as fast as they enter. Such a plant needs more nitrogen.

These variations indicate the need for some consideration, during interpretations of the tests, of the changing situations involved.

Investigators of soil fertility have not made as fast progress as possible because the "why of things" or the "how" and "why" of all the factors functioning in the performances of a growing crop have not always been given due consideration. In studying the nutritional status of crops, whether in fields, greenhouses, gardens, or flower pots, the investigator following a diagnostic procedure finds it necessary to examine and weigh all known factors before drawing conclusions. Since the supplies of nitrates, inorganic phosphates, and potash are the critical factors most frequently encountered, the diagnostician has gained much when the guessing about their adequacy is eliminated.

#### VALUE OF PLANT-TISSUE TESTS IN FERTILITY RESEARCH

Progress in fertility research is seriously handicapped as long as investigators are satisfied to ignore or to guess at the nutritional status within the growing crop. It would be a fallacy to argue that a technique exists that answers all

the nutritional questions; yet when the tissue-test method can indicate a "low" or "high" supply or a state of balance of nitrate, phosphate, or potash at an early stage of the plant growth, or throughout its growing period, it seems only common sense to consider such information valuable.

A typical case history is given in table 1 to show how the tissue tests aid in studying old fertility experiments.

One of the permanent general fertility experiments maintained by the Purdue Experiment Station has been running continuously since 1919. This field at Huntington, Indiana, includes a comparison of various sources of phosphates for crop production. Inasmuch as

TABLE 1

*Plant-tissue tests as an aid in the study of long-time fertility experiments in which various phosphate carriers are compared*

Tests made on corn at early tasseling stage, July 18, 1941, at Huntington, Indiana; data by M. T. Vittum

PLOT	TREATMENT*	PLANT-TISSUE TESTS			AVERAGE YIELD PER ACRE 1919-1940	1941 YIELD
		Nitrogen	Phosphorus	Potash		
1	None	High	Very low	Very low	bu. 36.1	bu. 26.8
3	BS	High	Low	Very low	38.4	45.1
4	SP	High	Low	Very low	37.6	49.3
5	RP	High	Low	Very low	34.2	43.7
7	L + BS	High	Very low	Very low	39.1	45.1
8	L + SP	High	Very high	Very low	39.3	36.6
9	L + RP	High	High	Very low	37.5	35.2
20	L Res. SP	High	Low	Very low	44.8	54.9
21	L Res. PK	High	Medium	Low	45.7	56.3

\* BS = 200 pounds of 18 per cent basic slag per acre on corn and wheat.

SP = 180 pounds of 20 per cent superphosphate per acre on corn and wheat.

RP = 480 pounds of 30 per cent rock phosphate per acre on corn and wheat.

L = 2 tons of ground limestone per acre applied in 1919.

Res. = Cornstalks and straw returned to the land.

PK = 300 pounds of 0-12-4 per acre on corn and wheat.

these phosphate plots were laid out at a time when it was believed that the soil could supply adequate quantities of potassium for normal plant growth, potash was not included in the treatments.

The results of the tissue tests, given in table 1, show that on the plots where various carriers of phosphates have been compared, potash has been the first limiting factor in the growth of corn. The yields of these plots have, therefore, been a function of the available potash instead of phosphorus, and the results obtained from the different phosphates are misleading. Plot 21, which had received some potash, was not receiving enough to supply the plants adequately.

As a result of these tissue tests the potash deficiency has been corrected by adequate additions of KCl; in the future, therefore, the yields will be a function of the phosphates used, and a true comparison of the different forms of phosphates will be obtained.

In recent investigations at Purdue much progress has been made in finding effective means of fertilizing corn directly on impoverished soils. A typical case history that illustrates this is presented in table 2.

Attention is directed to the following points brought out in table 2:

1. Phosphate was adequate in all plots; without the tissue tests, one would not be sure on this point.

2. In group I, the tissue tests show that nitrogen is the first limiting element, but as the rate of application of nitrogen is increased, potassium becomes limiting. Without the tissue tests, one might assume that the larger nitrogen treatments were not very effective.

TABLE 2

*Correlation of plant-tissue tests with rates of nitrogen and potassium fertilization treatments and yields of corn*

Data by H. L. Cook, on Crosby silt loam, Lafayette, Indiana, 1940

GROUP NO.	PLOT	MATERIALS FLOWED UNDER PER ACRE*		YIELD PER ACRE	YIELD INCREASE ABOVE TREATMENT 1‡	PLANT-TISSUE TEST‡					
						July 10			August 1		
		N†	K <sub>2</sub> O			N	P	K	N	P	K
		lbs.	lbs.	bu.	bu.						
I	1	0	0	29.5		0	H	H	0	H	M
	2	21	0	36.3	6.8	M	H	M	0	H	L
	3	42	0	49.4	19.9	H	H	L	M	H	0
	4	84	0	52.8	23.3	H	H	0	H	H	0
II	11	0	50	30.8	1.3	0	H	H	0	H	H
	5	21	50	49.4	19.9	L	H	H	0	H	H
	7	42	50	56.2	26.1	H	H	H	0	H	M
	9	84	50	68.1	38.6	H	H	H	H	H	M
III	12	0	100	33.8	4.3	0	H	H	0	H	H
	6	21	100	50.1	20.6	L	H	H	0	H	H
	8	42	100	59.3	29.8	H	H	H	0	H	H
	10	84	100	71.8	42.3	H	H	H	M	H	H

\* All plots received 300 pounds/acre of 0-16-4 in the fall at planting time.

† N was in form of calcium cyanamid. Similar data are available with N in the form of ammonium sulfate.

‡ Significant difference 3.2 bushels/acre.

§ 0, none; L, low; M, medium; H, high. Tests are an average of six plants from each of five replicates.

3. In group II, where 100 pounds of muriate of potash was plowed under with the nitrogen, it is apparent that nitrogen has become the limiting element except at the higher rates, where the adequacy of potash had become doubtful by August 1.

4. In Group III, where 200 pounds of muriate was used, the potash test shows an adequate supply and the yields then become a function of the nitrogen application. Here it is interesting to note that nitrogen had become limiting by August 1 and that higher rates of application probably would have produced additional corn.

The purpose of the research represented by table 2 was to find first, if possible, the boundaries of the nutritional factors necessary to produce an acceptable crop yield. The needs of the growing plant, regardless of treatment costs, were the

prime factors considered. To this end the plant-tissue technique was used. Some limitations in the experiments were exposed each season by these tissue tests, and corrections could be made for the next experiments. It was found that many assumptions, even old standard practices, were not measuring up to the requirements of the plants.

For example, during the 1940 season the plowing down of a phosphate fertilizer was compared with a similar application of phosphate in the row at planting time. In both cases the nitrogen and potash were plowed under. The season was characterized by a prolonged drought during July and August. Although the corn on the plowed-under fertilizer plot started slowly, it appeared more vigorous throughout the later part of the growing season. Plant-tissue tests were made on the corn plants the first week of August.

Exposure of a profile across the corn rows showed that very few active roots were in the very dry soil in which the row fertilizer was placed. On the other hand, there was an abundant growth of live roots in the moist soil at plow depth in which the plowed-under phosphate was placed. In this instance, the plant-tissue test aided in diagnosing the role of fertilizer placement in plant nutrition. Though the final yields showed that the

TABLE 3

*Plant-tissue tests as an aid in studying phosphate fertilizer placement for corn*

Data by A. J. Ohlrogge, on Crosby silt loam, Lafayette, Indiana, 1940

FERTILIZER TREATMENT PER ACRE		PLANT TISSUE TEST			YIELD PER ACRE
Plowed under	Drilled in row	N	P	K	
120 lbs. N 120 lbs. K <sub>2</sub> O	120 lbs. P <sub>2</sub> O <sub>5</sub>	VH	L	H	bu. 56.6
120 lbs. N 120 lbs. P <sub>2</sub> O <sub>5</sub> 120 lbs. K <sub>2</sub> O		H	H	H	67.3

phosphate placed in the row was not so effective as that plowed under, one would be inclined to assume that 120 pounds of P<sub>2</sub>O<sub>5</sub> per acre applied in the row would be more than enough phosphate for the corn. The tissue tests showed, however, that the plants were not getting it from the dry soil.

More rapid progress was made in the experiments by defining the nutritional boundaries involved, and much time in the annual replication of these experiments has been eliminated. With the optimum rate of nutrient supply and the method of placement accurately bounded, the next phase of the research was possible, that is, to find the most economical way to meet these requirements for the crops grown under specific soil conditions. This is being done in experiments that have been conducted the last 4 years in which heavy applications of fertilizers have been used to obtain the lowest cost units of production.

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# PRACTICAL APPLICATIONS OF POTASSIUM INTERRELATIONSHIPS IN SOILS AND PLANTS<sup>1</sup>

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The practical use of potash in crop production depends on the potassium requirement of the specific crop as related to the amount and quality of the product, on the ability of the soil to supply potassium to the plant, on the system of farming, and on the methods of fertilization. In this paper a few pertinent phases of the problem are briefly considered.

## POTASSIUM REQUIREMENT OF CROP

It is a well-known fact that plants differ in their potassium requirements. Most root crops, for example, require large amounts of potash for maximum development.<sup>2</sup> It has also been noted that legumes are more responsive to potash than are grasses. The importance of potash in legume production has been evidenced in fertilizer experiments at Purdue University,<sup>3</sup> in which the addition of potash to lime and phosphate or to lime alone increased alfalfa production by about 1000 pounds. Results from the North Carolina Piedmont have indicated a similar increase in the yield of red clover hay when potash was added to lime and phosphate. Cotton is another crop that responds to adequate potash fertilization. This fact is clearly shown in results obtained at the North Carolina Agricultural Experiment Station,<sup>4</sup> in which the addition of 50 extra pounds of potash increased the yield 445 pounds per acre, the addition of 7½ pounds per acre to nitrogen and phosphoric acid nearly doubled the yield of seed cotton on limed land, and the addition of 45 pounds caused an approximate threefold increase.

Not only is potash essential for increasing yields, but it also plays an important role in determining crop quality. The experiments with cotton previously mentioned showed that potassium increases the strength of the fiber and produces a higher percentage of lint per seed. Furthermore, experiments with flue-cured tobacco at the Oxford Branch Station in North Carolina gave the following outstanding results: 800 pounds of 5-8-0 per acre yielded 763 pounds having a value of \$71.42, whereas 800 pounds of 5-8-5 yielded 1,196 pounds with a value of \$191. In the field of horticultural crops, nearly everyone is familiar with the fact that the desired shape of good grades of sweet potatoes is obtained only in the presence of adequate potassium.

Crops, then, may be divided roughly into various groups with respect to their

<sup>1</sup> Contribution from the North Carolina Agricultural Experiment Station. Published with the approval of the director as a Paper of the Journal Series.

<sup>2</sup> R. I. Agr. Exp. Sta. Bul. 280, 1941.

<sup>3</sup> Purdue Univ. Cir. 242 (Revised): 10, May, 1941.

<sup>4</sup> N. C. Agr. Exp. Sta. Bul. 308 (1937) and 331 (1942).

potassium requirements. Legumes, root crops, cotton, tobacco, onions, and tomatoes usually give good responses to potash fertilization. Small grains, hay, and pasture grasses seem to show the least response to potash. Corn occupies an intermediate position. These facts must be kept in mind in interpreting the technical aspects of potassium-plant interrelationships in terms of practical application in the field.

#### POTASSIUM-SUPPLYING POWER OF SOILS

Soil differences are extremely important in determining the fertilization of any crop. Soils vary in their total potassium content, in the amount of readily available potassium, and in their ability to fix soluble potassium in unavailable forms. It is, perhaps, sufficient to show what difference might be expected in the potash responses of various soils. The work of the Illinois Agricultural Experiment Station is outstanding in this regard.<sup>5</sup> For example, corn from a rotation including corn, oats, wheat, and hay has consistently shown larger responses from potash than the small grains and the grasses. These results are very significant. Potash fertilization has varied in its effects from an 18.7-bushel increase per acre in corn yields on the Ewing field, a gray soil with an impervious noncalcareous subsoil, to a 2.9-bushel decrease on the Hartsburg field, a dark soil with a heavy calcareous subsoil. Moreover, the change in the total digestible nutrients produced varied from an increase of 640 pounds on the Ewing field to a decrease of 74 pounds on the Aledo field, a dark soil with a heavy noncalcareous subsoil. In general, the lower the fertility level of the soil, as shown by the yields on the no-treatment plots, the greater is the response from potash fertilization. There are several exceptions, however. For example, Oblong and Lebanon fields—the former soil similar to that of the Ewing field, and the latter a dark soil with a heavy, impervious, noncalcareous subsoil—gave the same yields on the check plot, but the former showed a 14.6-bushel increase with potash and the latter only 0.1 bushel. Also, comparison of the results from the Unionville and Dixon fields—the former, a yellowish gray soil with an impervious noncalcareous subsoil, and the latter a dark soil with an open noncalcareous subsoil—show that about the same increase in corn yields per acre was obtained with potash fertilization. The fertility level of the Dixon field, as evidenced by check-plot yields, was nearly four times that of the Unionville field. It is obvious, therefore, that differences in soils together with differences in crop requirements make it necessary to give considerable thought to the practical aspects of potash fertilization.

#### FARM MANAGEMENT SYSTEMS

The use of potash must be considered in relation to the system of farming and the management of the land. Even though crops vary in their needs for potassium, the use of potash on a particular crop must be considered in relation to previous crops and prior treatment of the soil. One cannot intelligently fertilize

<sup>5</sup> Ill. Agr. Exp. Sta. Bul. 425, 1936.

a crop *per se*. One must fertilize in a cropping system. This means the use of potash along with other nutrients, lime, and green manure crops. Legumes in the rotation may have several effects on the potash fertilization of the succeeding crops. In the first place, it has been shown that turning under large quantities of legumes may cause a disturbance of the potassium-nitrogen relationships which will result in decreased yields of the succeeding crops. This effect has been observed rather widely throughout the corn belt where sweet clover has been used as a green manure crop. A typical example of these effects is given in table 1. In a 2-year rotation of corn, wheat (sweet clover), the sweet clover plot yielded 23.5 bushels more corn per acre than the check plot the first year of the experiment. This differential decreased to 14.8 bushels for the second corn crop. After the third crop of sweet clover had been turned under, the yields were 21 bushels less than those on the check plot. The corn showed visible signs of potash defi-

TABLE 1  
*Effect of legume crops on potassium-nitrogen relationships\**

YEAR	YIELD OF CORN PER ACRE		
	No treatment	Manure	Sweet clover
	bu.	bu.	bu.
1924	47.3	51.3	70.8
1926	47.2	62.3	62.0
1928	64.8	63.0	43.8
1930	13.8	11.2	11.7
1932	44.4	55.5	45.5
1938†	34.7 (34.0)‡	43.5 (46.9)	47.7 (59.4)
1940	29.5 (30.7)	40.0 (44.9)	56.2 (65.8)

\* Sanborn field data, through courtesy of Missouri Agricultural Experiment Station.

† Drought in 1934 and 1936 caused complete failure of corn crop.

‡ Figures in parentheses are yields obtained with 400 pounds 0-12-12.

ciencies, with excessive lodging. After 1932, the experimental arrangement was changed to include a 400-pound application of 0-12-12 to one half of each of the plots. Yields on the fertilized half of the sweet clover plot approximated those of the first two corn years of the experiment.

The growing of legumes and the cutting of the entire crop for hay may result in large potash removals from the soil, which will accentuate the potash needs of the succeeding crop. This is especially true of those legume crops that do not leave an extensive root system in the soil. Soybeans, for example, may be either soil-conserving, if the entire crop is turned under, or soil-depleting, if the crop is removed for hay. This is true also for cowpeas and to a certain extent for lespedeza. Experiments at the North Carolina Station have shown that lower yields of corn are obtained following lespedeza or soybeans cut for hay than from land not seeded to these legumes. Certain areas in North Carolina that have been growing lespedeza as a hay crop for many years are showing severe potash deficiencies. One of the outstanding examples of potash removal by legumes is



with the peanut crop. When peanuts are harvested, the entire plant, including the tops, nuts, and roots, is removed from the soil. A yield of 2,000 pounds of nuts and 4,000 pounds of hay removes about 103 pounds of  $K_2O$  from the soil. The nuts remove nutrients equivalent to 175 pounds of an 0-8-12 fertilizer; the hay and nuts together remove nutrients equivalent to 300 pounds of an 0-8-34. Thus, the peanut is seen to be a severe sod-depleting crop. Crops following peanuts—generally corn or cotton—are usually poor, and experiments have shown that extra potash fertilization is essential. To illustrate these difficulties more clearly, a 4-8-4 fertilizer is commonly used for cotton in the North Carolina Coastal Plain. The potash removed from the soil by the peanut crop described above is equivalent to that carried in 2,575 pounds of a 4-8-4 fertilizer.

Calcium-potassium relationships are extremely important in crop production. Liming may have various effects on potash fertilization. In general, on soils

TABLE 2

*Average loss of exchangeable potassium from the surface 4 inches of Creedmoor coarse sandy loam between November 6, 1940, and January 10, 1941\**

SOIL pH	BASE SATURATION	EXCHANGEABLE POTASSIUM
	<i>per cent</i>	<i>per cent</i>
4.83	28	70
5.08	37	61
5.30	40	49
5.63	50	26
6.32	65	24
7.03	72	16

\* Data from outdoor pot studies at the North Carolina Agricultural Experiment Station; rainfall 6.2 inches.

that have low potassium reserves, liming increases the need for potash. This is particularly true where legumes are grown. A typical example of the effect of lime on the returns from potash is found in data obtained on a Piedmont soil in North Carolina,<sup>6</sup> on which the rotation was cotton, corn, wheat, red clover. These data disclose that liming decreased the cotton yields on those plots where the potassium level was low. On plots where the potassium level with respect to phosphorus was higher, the cotton yields were increased by liming. It is significant that the clover yields were relatively large on all the limed plots. Undoubtedly, the removal of potash from the soil by the hay crop has been responsible in large measure for the decreased cotton yields. Other calcium-potassium relationships are also involved. The net result, however, has been to increase the potash needs of cotton and corn by the use of lime and legumes in the rotation.

Other experimental evidence in North Carolina on the fertilization of peanuts

<sup>6</sup> N. C. Agr. Exp. Sta. Bul. 331.

indicates that the effects of potash are determined primarily by the calcium and magnesium present. Shelling percentages and oil content seem to be correlated with the correct balance between these two nutrients.

Liming the rotation plays another important role in potash relationships. Experiments on sandy tobacco soils have shown that loss of potassium is determined to a great extent by the degree of base saturation. The more acid the soil and the lower the degree of base saturation, the greater is the removal of exchangeable potassium by leaching. These results are given in table 2. It is seen that 70 per cent of the available potassium was lost from this soil at a pH of 4.83 and 28 per cent base saturation. At the neutral point, with 72 per cent saturation, only 16 per cent of the potash was lost. Field results confirm these data from outdoor pot experiments. The practical significance of these findings is extremely important in tobacco production. Tobacco is generally grown on nonlimed soils. Most of the potash is applied prior to planting. Excessive rains undoubtedly remove considerable quantities of the applied potash. Consequently, insufficient potash may be present under these conditions to produce the desired quality in flue-cured tobacco.

#### METHODS OF FERTILIZATION

A knowledge of the needs of the crop, an analysis of the potash status of the soil, and consideration of the system of farming may indicate that a certain amount of potash is necessary for maximum results. The question of the method of application, however, must also be taken into consideration. If the soil is sandy and if the conventional method of placing fertilizer in the row is practiced, then excess soluble salts may definitely injure the stand. This is particularly true with tobacco, cotton, and peanuts.

Experimental results and experiences of farmers have indicated that applications of fertilizer in the row on the sandy soils of the Coastal Plain should be limited to a maximum of 6 per cent  $K_2O$  to prevent risk of injury to the crop. This effect is associated with the ready solubility of potash salts. Several practical solutions to these difficulties have been worked out. The experiment stations have demonstrated the value of side placement to overcome stand injury and to increase the efficiency of the applied fertilizers. Suitable equipment has been devised to obtain good side placement. The use of such machines, however, is rather limited at the present. Farmers are using side-dressings to supply the extra potash. Such side-dressings may be muriate of potash, a split application of the same fertilizer applied in the row, or a specially prepared side-dressing containing nitrogen and potash, or perhaps nitrogen, phosphoric acid, and potash. The rapid mobility of potassium from the surface to the root zone makes such a practice very satisfactory.

More research is needed on the advisability of applying potash fertilizers to the soil when it is plowed. It would seem that the success of such a method would be related to the type of soil, the type of crop being turned under, and the type of crop to be planted.

## CONCLUSIONS

In conclusion, it should be reemphasized that plant-potassium and soil-potassium interrelationships have concrete practical application to the problems of agriculture. For most efficient crop production, technical knowledge must be tied in with a thorough understanding of the crop, the soil, the farming system, and the method of fertilizing.

# THE EFFECT OF CARBON DIOXIDE ON SOIL REACTION

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Soil structure, solubility of minerals, growth of microflora, adsorption of minerals by plants, and many other physical, chemical, and biological processes are known to be affected by the acidity or alkalinity of the soil system. Soil reaction studies, therefore, are of major interest to soil investigators.

The soil is a heterogeneous mass, varying in composition from place to place, and is affected variably by an uneven distribution of plant roots, microflora, and other organic materials. Environmental factors such as temperature, moisture, and air are also variable with respect to both time and space within the soil mass. Soil reaction, therefore, is not a constant property of any soil but a function of many factors. The degree of change in reaction at any point within the soil is dependent upon the buffer capacity of the compounds inherent in the soil mass as well as upon changes in the environment.

Because the soil reaction in the immediate vicinity of the plant roots is likely of greatest importance to plant growth, an ultimate goal of soil reaction studies probably should be the determination of pH at the plant-root and soil contacts. Because of variations of  $\text{CO}_2$  pressure with position along the plant-root system and with time of day or other growth conditions of the plant, the pH at these contact points probably is not constant. It would be necessary, therefore, to express the pH of the system either as numerous individual data representing many contact points or as a continuous function of the  $\text{CO}_2$  pressure within the limits found in the soil. If it is to be expressed as a function of the  $\text{CO}_2$  pressure, then the same result as measuring pH at the root contacts should be accomplished by equilibrating soil samples with various pressures of  $\text{CO}_2$  and determining the pH of the systems. The extreme limits of the  $\text{CO}_2$  pressure should lie between the partial pressure due to  $\text{CO}_2$  in the air above the soil and an atmosphere of  $\text{CO}_2$ .

Since carbon dioxide, bases, and water are always present in natural soils, it is convenient to consider the soil as a simple case of a ternary system, base- $\text{CO}_2$ - $\text{H}_2\text{O}$ . All three components can vary from low to rather high levels, depending upon the soil, climate, and other conditions. Equilibrium in carbonate systems cannot exist unless all three components are constant. These being constant, the ratios among  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ , and  $\text{H}_2\text{CO}_3$  are constant, and the pH is constant. A change in environment of a soil, especially in the soil atmosphere, easily can change the proportions of the components. If the soil is disturbed by sampling, a subsequent analysis of the disturbed soil system for bases, carbonates, bicarbonates, or hydrogen-ion concentration will not reflect the levels of these constituents in the undisturbed soil.

These components in a large mass of soil may never be at one equilibrium, but there may be innumerable loci of near-equilibria, all of which are different. Field soils *in situ* probably have, not a single hydrogen-ion concentration, but a series

of concentrations depending upon the base- $\text{CO}_2$ - $\text{H}_2\text{O}$  system in a particular spot. If the predominating base is  $\text{CaCO}_3$ , as is the case in calcareous soils, then the pH at any  $\text{CO}_2$  pressure might be expected to be about the same as the pH of a  $\text{CaCO}_3$  suspension. The presence of  $\text{MgCO}_3$ ,  $\text{Na}_2\text{CO}_3$ , or other bases, a very low base content, the type of clay minerals, or organic matter naturally would result in different pH values.

Many studies have been made of the effects of carbon dioxide, water, and other factors on soil reaction (1, 2, 4, 8, 9, 12, 13, 14, 15, 16, 17, 20). Simmons (19) and Bradfield (3) have studied a clay- $\text{CaCO}_3$ - $\text{CO}_2$ - $\text{H}_2\text{O}$  system, but few attempts have

TABLE 1  
*Carbonate content, moisture equivalent, and normal field capacity of some soils from western states*

SOIL	$\text{CO}_2$	LIME	MOISTURE EQUIVALENT	NORMAL FIELD CAPACITY
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
1. Slick spot, Montrose, Colo.*.....	10.97	24.93	28.33	30.00
2. Weld series, northern Colo.†.....	0.50	1.15	21.39	25.21
3. Neville series, northern Colo.†.....	0.03	0.07	23.84	28.24
4. Terry series, northern Colo.†.....	0.02	0.04	12.08	20.42
5. Fort Collins series, northern Colo.†.....	1.59	3.61	21.49	24.37
6. Cass clay, northern Colo.†.....	0.93	2.16	31.31	32.16
7. Mohave soil, Arizona†.....	4.10	9.32	.....	32.50
8. Gila soil, Arizona*.....	1.83	4.17	.....	32.50
9. Kearney plot soil, San Joaquin Valley, Calif.*..	0.21	0.48	.....	20.00
10. Same as 9, after reclamation†.....	0.02	0.05	.....	17.50
11. Arizona soil, series not known†.....	0.16	0.37	.....	35.00
12. Utah soil, 2-6 inches†.....	14.89	33.85	.....	45.00
13. Berthoud series, northern Colo.†.....	0.75	1.71	22.15	33.33
14. Baca County subsoil, southeastern Colo.†.....	0.02	0.05	15.24	21.76
15. Alpine meadow, Estes Park, Colo.†.....	0.02	0.05	18.90	27.06
16. Johnstown terrace soil, northern Colo.†.....	1.79	4.07	20.09	27.03
17. Phosphorus-deficient soil, northern Colo.†.....	2.22	5.05	15.86	25.04
18. White alkali soil, northern Colo.†.....	3.01	6.84	24.53	31.87

\* Black alkali soils—calcareous.

† Calcareous soils—Na low.

‡ Do not effervesce with dilute acid.

been made to determine quantitatively the effect of water content and the carbon dioxide concentration on soil reaction in natural soils. This paper is a report of a study of pH changes as a result of changes in carbon dioxide pressure and soil-water ratio.

#### MATERIALS AND METHODS

Twenty-three soil samples and samples of calcium and magnesium carbonate were studied in the experiments. Table 1 gives the source of 18 of the samples, their carbonate content, the moisture equivalent, and the normal field capacity (18). Samples 1 to 6 and 13 to 18 are from Colorado, and samples 7 to 12 are

from other western states.<sup>1</sup> In addition, Baker's C.P. calcium and magnesium carbonates were studied.

All pH measurements were made with the Beckman pH meter, employing the regular Beckman internal glass electrode assembly, the Beckman industrial external glass electrodes, or specially constructed external glass electrodes. The specially constructed electrodes were 8 inches long and of small diameter so that they could be inserted into large test tubes through holes in a stopper. For soils at low moisture, the method of pH determination described by Haas (6) was followed. A constant temperature of 25° C. was maintained throughout the experiments.

The gas mixtures containing various concentrations of CO<sub>2</sub> were prepared in the early experiments by the method proposed by Johnston and Walker (10). Though the mixtures were approximately constant in composition, some variability occurred from day to day. In later experiments, the gas mixtures were prepared by passing known amounts of CO<sub>2</sub> into the tank of an air compressor, of the type used in gasoline service stations, which was then filled with air to the desired pressure. At the rate of use in these experiments, the tank held sufficient gas to last for 6 to 7 days. The gas mixtures in either case were analyzed daily and the CO<sub>2</sub> pressures calculated (10). Constant flow of the gas mixtures through the soil samples was obtained by first passing the gas through a flowmeter with a stopcock on the exit side (10).

Soil suspensions having soil to water ratios of 1 to 2, 1 to 5, and 1 to 10 were prepared. These were equilibrated at 25° C. with air containing various proportions of CO<sub>2</sub>. A continuous stream of the mixed gas was bubbled through distilled water to saturate it and then through the soil suspensions. Batteries of six aerators in series were used at a time. The gas was analyzed daily for CO<sub>2</sub>, and the results were corrected for the water vapor pressure and head of water above the gas outlets in the soil suspension tubes. While the gas was bubbling through the suspensions, the pH of each was determined daily by inserting suitable electrodes. Equilibrium was reached in 2 to 3 days with the high CO<sub>2</sub> pressures, and after 5 to 7 days with the lower pressures. Identical pH readings on two consecutive days were taken as the criteria of equilibrium.

## RESULTS

The effect of CO<sub>2</sub> pressure on the pH of the systems CO<sub>2</sub>-CaCO<sub>3</sub>-H<sub>2</sub>O and CO<sub>2</sub>-MgCO<sub>3</sub>-H<sub>2</sub>O is shown in figure 1. The curve for CaCO<sub>3</sub> includes values calculated from the data of Frear and Johnston (5) as well as from direct pH determinations. Reference to the original data of Frear and Johnston and of Kline (11) will show the variations in cation and anion concentrations for CaCO<sub>3</sub> and MgCO<sub>3</sub> systems as the CO<sub>2</sub> pressure varies. The equation of Simmons (19),  $\text{pH} = \text{p}K_1 - 0.5\sqrt{\mu} + \log(\text{HCO}_3^-) - \log(\text{H}_2\text{CO}_3)$ , when applied to the data of Frear and Johnston gave pH values agreeing closely with the observed value shown in

<sup>1</sup> These six soils were obtained through the courtesy of W. T. McGeorge, of the University of Arizona, and are from a group of soils used in a study of the technique of pH determination by McGeorge and Martin (15).

figure 1. The same equation applied to the  $\text{MgCO}_3$  data of Kline did not agree with the observed value shown in the table. Therefore, only the observed values for  $\text{MgCO}_3$  are shown.

Data showing the effect of variations in water content and  $\text{CO}_2$  pressure for 18 soils are given in table 2. In figure 2, the pH values of six of the soils, of  $\text{MgCO}_3$ , and of  $\text{CaCO}_3$  have been plotted against atmospheres  $\text{CO}_2$ . The curves differ more in their position on the pH scale than in shape. A striking feature of all the curves is the rapid drop in pH for small changes in  $\text{CO}_2$  at low pressures.

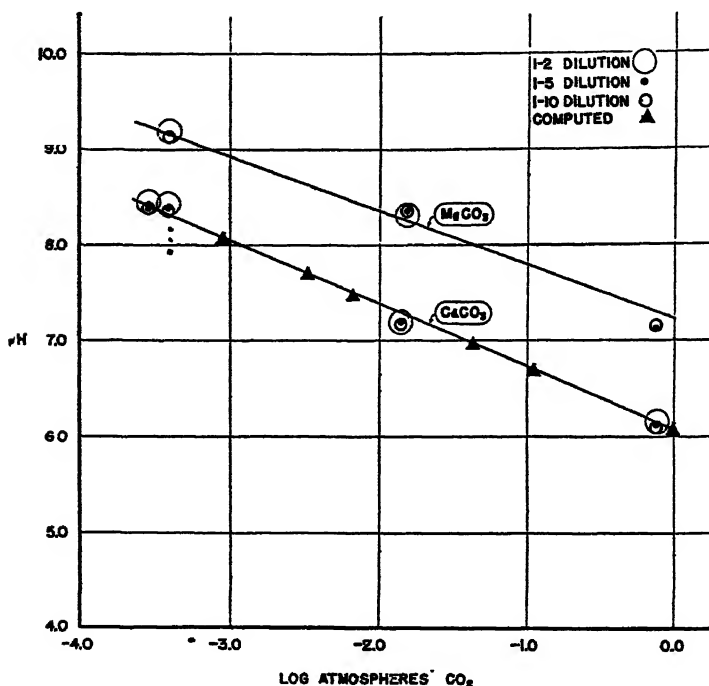


FIG. 1. THE pH OF CALCIUM AND MAGNESIUM CARBONATE SUSPENSIONS PLOTTED AGAINST THE LOG OF  $\text{CO}_2$  PRESSURE

The equation given by Simmons (19),  $\text{pH} = \text{p}K_1 - 0.5 \sqrt{\mu} + \log (\text{HCO}_3^-) - \log (\text{H}_2\text{CO}_3)$ , and the data of Frear and Johnston (5), were used to determine the computed  $\text{CaCO}_3$  curve.  $K_1$ , in the equation, is the dissociation constant, of the first hydrogen of  $\text{H}_2\text{CO}_3$ , and  $\mu$  is the ionic strength of the system. An adequate theoretical formula for computing the  $\text{MgCO}_3$  curve from the data of Kline (11) was not available.

The greatest reduction occurs below 3 per cent  $\text{CO}_2$ . The pH change above 0.03 atmosphere is very gradual. Carbon dioxide pressures above 0.03 atmosphere cause an acid reaction in all  $\text{Na}_2\text{CO}_3$ -free soils studied. Considerably lower  $\text{CO}_2$  pressures than this produced an acid reaction in the noncalcareous soils. The effectiveness of  $\text{CO}_2$  over the lower pressure range in reducing the pH of soils is evident from the curves. The data probably explain the low pH values often observed in calcareous soils when the measurements are made *in situ* (7). The similarity between the soil curves and the calcium and magnesium carbonate

TABLE 2  
*Effect of CO<sub>2</sub> on pH of soil suspensions*

SOIL NUMBER	1 SOIL TO 2 WATER		1 SOIL TO 5 WATER		1 SOIL TO 10 WATER	
	<i>atmospheres</i>	<i>pH</i>	<i>atmospheres</i>	<i>pH</i>	<i>atmospheres</i>	<i>pH</i>
1	.00025	9.03	.00025	9.00	.00025	8.90
	.00042	8.93	.00042	8.85	.00042	8.63
	.01409	7.90	.01409	7.66	.01405	7.60
	.02914	7.53	.....	....	.....	....
	.09687	7.06	.....	....	.....	....
	.77893	6.40	.76826	6.38	.76826	6.28
2	.00034	8.37	.00037	8.08	.00039	7.92
	.02914	7.01	.....	....	.....	....
	.09687	6.65	.....	....	.....	....
	.77893	6.08	.76679	5.94	.76751	5.88
3	.00034	6.88	.....	....	.....	....
	.02914	6.28	.....	....	.....	....
	.09687	6.00	.....	....	.....	....
	.77893	5.70	.....	....	.....	....
4	.00034	8.06	.00037	7.29	.00039	7.21
	.02914	6.77	.....	....	.....	....
	.09687	6.38	.....	....	.....	....
	.77893	5.71	.76679	5.37	.76751	5.08
5	.00025	8.20	.00037	8.03	.00039	7.90
	.00042	8.11	.00042	7.98	.00042	7.96
	.00070	8.03	.....	....	.....	....
	.00519	7.36	.....	....	.....	....
	.02914	7.00	.....	....	.....	....
	.09687	6.61	.....	....	.....	....
	.77893	6.04	.76679	5.92	.76751	5.83
6	.00070	7.88	.....	....	.....	....
	.00519	7.43	.....	....	.....	....
	.09687	6.70	.....	....	.....	....
	.77893	6.13	.....	....	.....	....
7	.00031	8.30	.....	....	.....	....
	.00062	8.12	.....	....	.....	....
	.00070	7.98	.....	....	.....	....
	.00519	7.43	.....	....	.....	....
	.11259	6.66	.....	....	.....	....
	.76780	6.13	.....	....	.....	....
	.77278	6.11	.....	....	.....	....
8	.00030	9.20	.00030	9.03	.00030	8.90
	.00062	8.96	.....	....	.....	....
	.01300	7.86	.01300	7.62	.01300	7.52
	.05372	7.42	.....	....	.....	....
	.11259	7.09	.....	....	.....	....



TABLE 2—(Continued)

SOIL NUMBER	1 SOIL TO 2 WATER		1 SOIL TO 5 WATER		1 SOIL TO 10 WATER	
	<i>atmospheres</i>	<i>pH</i>	<i>atmospheres</i>	<i>pH</i>	<i>atmospheres</i>	<i>pH</i>
	.15136	6.99	.15136	6.78	.15136	6.68
	.76365	6.32	.76365	6.12	.76365	6.05
	.76780	6.39	.....	....	.....	....
	.77273	6.39	.....	....	.....	....
9	.00062	8.85	.....	....	.....	....
	.00070	8.72	.....	....	.....	....
	.05372	7.34	.....	....	.....	....
	.11259	6.98	.....	....	.....	....
	.76780	6.31	.....	....	.....	....
	.77278	6.28	.....	....	.....	....
10	.00031	8.29	.....	....	.....	....
	.00062	8.20	.....	....	.....	....
	.00519	7.35	.....	....	.....	....
	.11259	6.37	.....	....	.....	....
	.76780	5.70	.....	....	.....	....
	.77278	5.67	.....	....	.....	....
11	.00031	8.63	.00037	8.07	.00039	7.95
	.00062	8.42	.....	....	.....	....
	.05372	6.86	.....	....	.....	....
	.11259	6.72	.....	....	.....	....
	.76780	6.19	.76679	5.88	.76751	5.67
	.77278	6.20	.....	....	.....	....
12	.00031	8.19	.....	....	.....	....
	.00070	7.95	.....	....	.....	....
	.00519	7.48	.....	....	.....	....
	.11259	6.83	.....	....	.....	....
	.76780	6.23	.....	....	.....	....
	.77278	6.26	.....	....	.....	....
13	.00029	8.13	.....	....	.....	....
	.02453	7.05	.....	....	.....	....
	.10938	6.70	.....	....	.....	....
	.77278	6.13	.....	....	.....	....
14	.00029	7.50	.....	....	.....	....
	.02453	6.41	.....	....	.....	....
	.10938	6.20	.....	....	.....	....
	.77278	5.69	.....	....	.....	....
15	.00029	7.07	.....	....	.....	....
	.02453	6.35	.....	....	.....	....
	.10938	6.20	.....	....	.....	....
	.77278	5.78	.....	....	.....	....

TABLE 2—(Concluded)

SOIL NUMBER	1 SOIL TO 2 WATER		1 SOIL TO 5 WATER		1 SOIL TO 10 WATER	
	<i>atmospheres</i>	<i>pH</i>	<i>atmospheres</i>	<i>pH</i>	<i>atmospheres</i>	<i>pH</i>
16	.00029	8.30	.00039	8.20	.....	....
	.00030	8.20	.00037	8.00	.00039	7.88
	.00070	8.09	.....	....	.....	....
	.02453	7.08	.....	....	.....	....
	.10938	6.69	.....	....	.....	....
	.76883	6.15	.76883	6.09	.76883	6.07
	.77273	6.11	.....	....	.76751	5.91
17	.00029	8.03	.....	....	.....	....
	.02453	7.02	.....	....	.....	....
	.10938	6.75	.....	....	.....	....
	.77273	6.14	.....	....	.....	....
18	.00029	8.22	.....	....	.....	....
	.00030	8.22	.....	....	.....	....
	.00067	8.21	.....	....	.....	....
	.01300	7.29	.....	....	.....	....
	.02453	7.32	.....	....	.....	....
	.10938	6.98	.....	....	.....	....
	.76365	6.31	.....	....	.....	....
	.77278	6.35	.....	....	.....	....

curves is evident. The calcareous soils with  $\text{Na}_2\text{CO}_3$ , the moderately or highly calcareous soils without  $\text{Na}_2\text{CO}_3$ , and the slightly calcareous or acid soils, however, seem to fall into three distinct families of curves, similar in shape but with somewhat different positions on the pH scale. The  $\text{Na}_2\text{CO}_3$  soils are highest on the pH scale and have the steepest slopes. The calcareous soils without  $\text{Na}_2\text{CO}_3$  are intermediate. The  $\text{MgCO}_3$  lies much higher than any of the soils studied and suggests that  $\text{MgCO}_3$  soils might form a fourth family of curves with a high pH.

When the pH data from table 2 are plotted against the logarithm of the atmospheres  $\text{CO}_2$ , as shown in figure 3, a straight line is obtained for each soil when the ratio of soil to water is held constant. From these data it is evident that two carefully determined points for each soil are sufficient to plot a curve showing the effect of  $\text{CO}_2$  pressure on the pH of the system at constant moisture in the moisture range studied. Figure 3 shows the curves for the 18 soils. The curves of the computed (5, 19) and the experimentally determined pH values for  $\text{CaCO}_3$  at three dilutions and of the experimental values for  $\text{MgCO}_3$ , at corresponding dilutions, plotted against the logarithms of the  $\text{CO}_2$  pressures (fig. 1), indicate that the pH of the pure carbonate suspensions depends upon the  $\text{CO}_2$  pressure and is not appreciably affected by dilution. The same fact is shown more clearly in figure 4.

The effect of dilution of soil systems with water is more complicated than that of dilution of pure carbonate systems. At higher dilutions, the solid phase of some compounds in the soil system may disappear or the base-exchange status

may change, causing a change in pH, which would not occur in a pure carbonate system with an excess of solid phase. The pH of some of the soils was definitely lowered at constant  $\text{CO}_2$  pressure by increasing the dilution. This fact is shown by the data in table 2. The data on the effect of dilution, however, cover only the range between 200 and 1,000 per cent water and furnish no information in the low moisture range.

The task of equilibrating a soil system with  $\text{CO}_2$  is much more easily accomplished in suspensions of soil in water than in moist soil, but information regarding

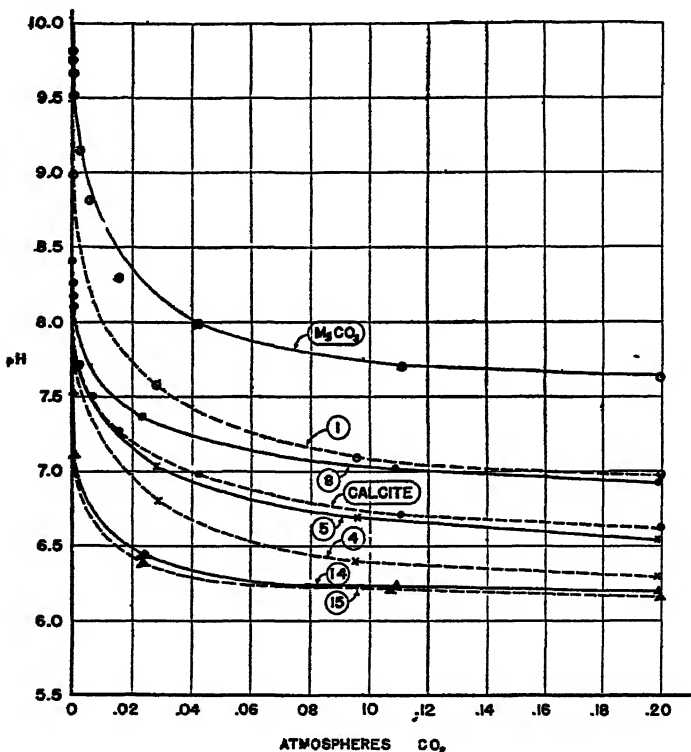


FIG. 2. EFFECT OF INCREASING  $\text{CO}_2$  PRESSURE ON THE pH OF CALCIUM AND MAGNESIUM CARBONATES AND SIX SOILS

The numbers on the graph refer to the soil numbers in table 1

the effect of  $\text{CO}_2$  pressure on pH in the moist soils is of more importance to agriculture. The possibility of extrapolating the data obtained from suspensions to moist soils was, therefore, investigated.

Enough  $\text{CO}_2$  is absorbed by air-dry soil samples to affect the pH appreciably when the soils are brought into suspension in water. By comparing the pH of suspension of soils in  $\text{CO}_2$ -free water with curves showing the pH as a function of  $\text{CO}_2$  pressure at the same dilution, it is possible to calculate the amount of  $\text{CO}_2$  in the sample. For example, if

$$\text{pH} = b \log \text{CO}_2 + k$$

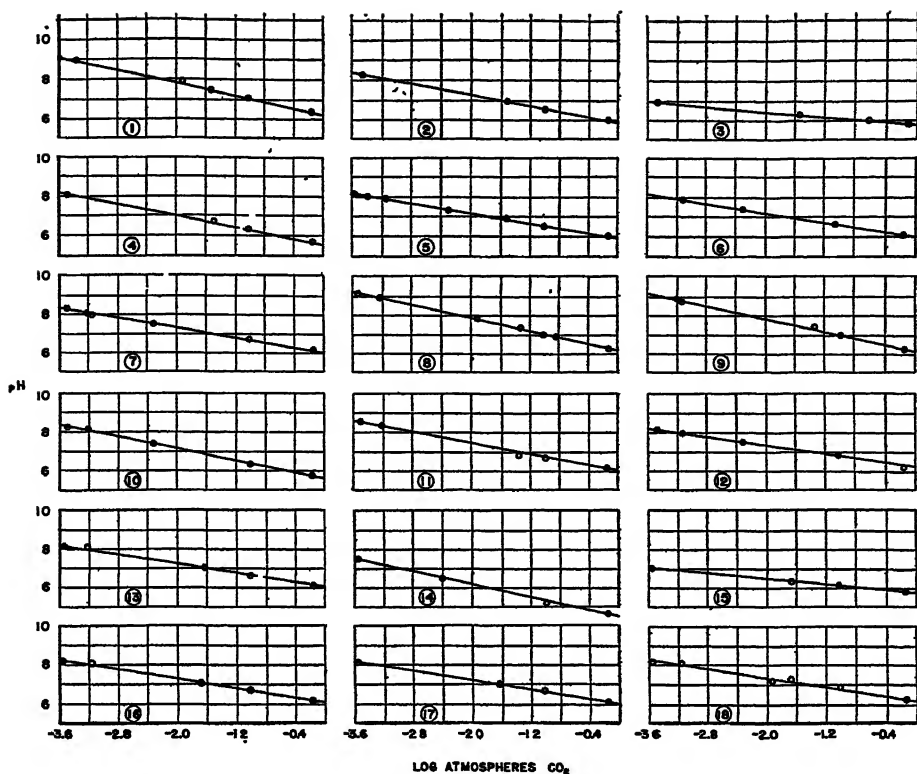
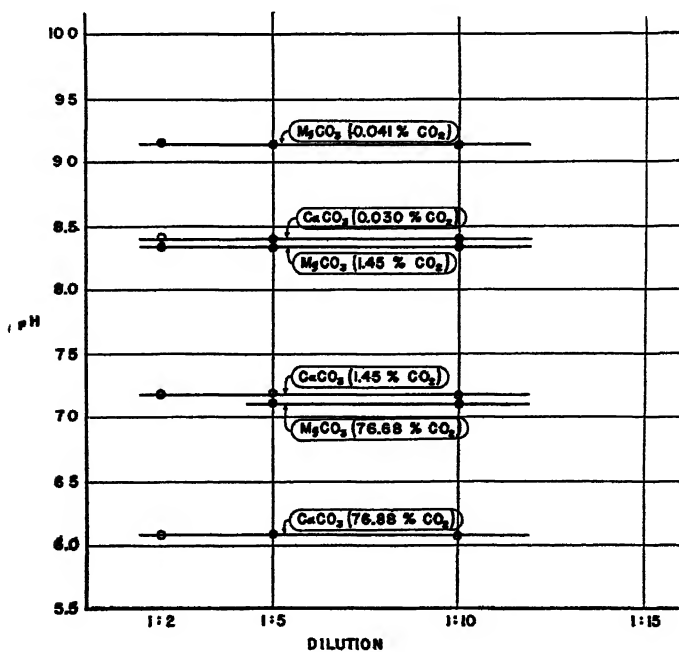


FIG. 3. THE pH OF 18 SOILS PLOTTED AGAINST THE LOGARITHM OF THE  $\text{CO}_2$  PRESSURE  
The soil to water ratio was 1 to 2



where  $b$  is the regression coefficient and  $k$  a constant, by substituting an experimentally determined pH value for the same soil at the same dilution into the equation, the  $\text{CO}_2$  pressure can be calculated. Following this reasoning, samples of the 18 soils described in table 1 were treated with distilled water and the pH values determined at the four dilutions, as shown in table 3. The  $\text{CO}_2$  pressure at 200 per cent water (1 to 2 dilution) was then calculated from the equation of curves in figure 3 ( $\text{pH} = b \log \text{CO}_2 + k$ ). On the basis of the assumption that the  $\text{CO}_2$  pressure varied inversely with the dilution, the pressures at the moisture equivalent, at 500 per cent water, and at 1,000 per cent water were also calculated. These values were then substituted into the equations and the corre-

TABLE 3  
*Observed and calculated pH values of soils at various soil to water ratios*

SOIL NUMBER	MOISTURE EQUIVALENT		1-2 DILUTION	1-5 DILUTION		1-10 DILUTION		r*
	Calculated pH	Observed pH	Observed and calculated pH	Calculated pH	Observed pH	Calculated pH	Observed pH	
1	9.19	9.6	9.9	10.20	10.2	10.43	10.7	.928
2	7.44	7.5	8.1	8.37	8.2	8.58	8.5	.927
3	6.27	6.3	6.6	6.74	6.6	6.85	7.0	.937
4	6.75	7.2	7.6	7.88	7.7	8.09	7.9	.991
5	7.10	7.6	7.7	7.95	8.1	8.13	8.5	.866
6	7.54	7.7	8.0	8.23	8.2	8.45	8.4	.994
7	7.69	7.4	8.2	8.44	8.3	8.65	...	.973
8	9.63	10.0	10.3	10.64	10.5	10.89	...	.985
9	9.51	9.9	10.2	10.47	10.4	10.68	...	.979
10	7.09	7.6	7.9	8.21	8.1	8.45	...	.977
11	7.80	7.8	8.3	8.58	8.4	8.79	...	.973
12	7.53	7.6	7.9	8.13	8.1	8.30	...	.680
13	7.44	7.8	8.0	8.23	8.2	8.41	8.4	.894
14	6.51	6.7	7.1	7.30	7.1	7.47	7.5	.936
15	6.62	6.5	7.0	7.15	7.1	7.26	7.2	.994
16	7.26	7.6	7.9	8.15	8.2	8.35	8.6	.941
17	7.36	7.8	8.0	8.23	8.2	8.41	8.5	.918
18	7.62	8.0	8.1	8.32	8.2	8.49	8.4	.908

\* The coefficient of correlation between the calculated and the observed pH for each soil.

sponding pH values obtained. These computed results are shown in table 3, together with the correlation coefficients between the computed and the observed values. The observed and the calculated results do not agree perfectly, though the agreement is close. In most cases the computed results are too low at the moisture equivalent.

It is evident that this method of extrapolation does not take into account the effect of dilution on any constituents, except  $\text{CO}_2$ , affecting pH. For that reason, the computed and the experimental curves could not be expected to fit perfectly. With the hope of getting a better fit, equations involving pH changes due to change in both  $\text{CO}_2$  pressure and dilution of other soil constituents were derived

from the data in table 2. The equations, which were of the form,  $H = b \log CO_2 + C \log H_2O + k$ , failed to fit the experimental data as well as the first equation. The correlation coefficients between the computed and the observed pH values for soils 1, 2, 4, and 5 were .93, .61, -.91, and .92, respectively. For

TABLE 4  
*pH Values of soil under varying conditions*

SOIL SAMPLE AND DEPTH	1 MOISTURE IN SAMPLE	2 SOIL IN SITU	3 SAME AS 2, EXCEPT EVACUATED FOR 17 HOURS	4 SAME AS 2, BUT DILUTED TO 1-2	5 SOILS OVEN-DRIED AND BROUGHT TO FIELD CAPACITY	6 SAME AS 5, BUT AFTER 50 DAYS IN HUMIDITY BOX
	<i>per cent</i>	<i>pH</i>	<i>pH</i>	<i>pH</i>	<i>pH</i>	<i>pH</i>
West Farm, Colo. Exp. Sta., 3 inch depth.....	20.34	7.00	7.80	8.02	7.42	7.37
White alkali, N. Colo., 3 inch depth...	27.81	7.60	8.12	8.32	7.75	7.80
Rocky Ridge school plot						
3 inch depth.....	10.96	6.70	7.40	8.34	7.03	7.23
12 inch depth.....	13.05	6.51	6.99	8.07	6.97	7.03
Havre series,* N. Colo., 3 inch depth..	57.33	7.09	8.27	8.29	8.11	7.84
East Farm, Colo. Exp. Sta.						
3 inch depth.....	21.48	7.20	7.80	8.06	7.62	7.60
12 inch depth.....	19.70	7.10	7.81	8.34	7.75	7.38

\* Very high in organic matter.

TABLE 5  
*Effect of aeration on pH of soil*

TIME	SOIL OPEN TO AIR	SOIL SEALED WITH PARAFFIN
<i>days</i>	<i>pH</i>	<i>pH</i>
1	7.68	7.70
2	7.57	7.53
3	7.59	7.48
4	7.60	7.42
5	7.59	7.41
6	7.62	7.38
8	7.61	7.30
9	7.56	7.28
10	7.52	7.23
24	7.52	7.21
24*	7.60	7.55

\* Following evacuation for 3 hours.

soils 1 and 5, where the dilution effect was slight at constant  $CO_2$  pressure, a fair fit was obtained, but for soil 4, with a large dilution effect, the observed and the computed values were negatively correlated. The fact that the observed and the calculated data fit so well when only the effect of diluting the  $CO_2$  is considered indicates that the major effect of dilution in the lower moisture range is due to

dilution of the  $\text{CO}_2$  present in the sample. Apparently the pH is not a straight-line function of the log of the percentage of water at constant  $\text{CO}_2$  pressure over the entire range from the moisture equivalent to 1,000 per cent water. More information is necessary on this phase of the problem.

The low pH observed in the field in many calcareous soils at low moisture probably can be explained to a large extent by a high  $\text{CO}_2$  pressure. This fact is further supported by tables 4, 5, and 6. In table 4, column 2, are presented the pH values of soils in the field under normal field moisture. In column 3, the pH values of samples of these soils, after being removed to the laboratory in a closed vessel over water and evacuated for 17 hours, are shown. No appreciable change in soil moisture occurred during the process. The rise in pH can be explained only by the fact that the  $\text{CO}_2$  pressure was greatly lowered. The pH rise after evacuation of air varied from 0.48 to 1.18 units.

In table 5 a moist soil sealed from the air is compared to another sample of the same soil under the same conditions except that it was exposed to the air. In 24 days, the sealed soil dropped 0.49 unit compared with a 0.16-unit drop for the

TABLE 6  
*Effect of time of standing on pH of several soils*  
(1-5 Dilution)

TIME	SOIL 5	SOIL 1	SOIL 4	SOIL 18
<i>days</i>				
1	8.00	10.08	8.23	8.51
2	7.72	9.90	8.03	8.40
3	7.70	9.82	8.00	8.16
4	7.70	9.49	7.82	8.18
5	7.64	9.42	7.69	8.13
6	7.63	9.40	7.65	8.10

aerated soil. After the vessel was evacuated and the  $\text{CO}_2$  pressure reduced, the pH values of the two samples were almost identical. Under anaerobic conditions organic acids other than carbonic might have been responsible for the lowering of the pH, but they would not have been removed by the process of evacuating the vessel of gases.

In table 6 the effect of standing 6 days in suspension is shown for four soils. The pH at the end of the period was approximately what it would have been after equilibrating with the  $\text{CO}_2$  of the laboratory air.

#### DISCUSSION

Data have been presented which show that variations in carbon dioxide concentration in a system consisting of soil, water, and carbon dioxide create comparatively large changes in hydrogen-ion concentration. In view of the fact that under field conditions carbon dioxide and the compounds formed with soil materials and water are always present in the soil solution and that the carbon dioxide pressure varies over a wide range in the soil it is evident that pH is far

from a constant in the system. Carbon dioxide is, of course, not the only variable factor upon which soil reaction depends, but for any particular soil, carbon dioxide and water probably fluctuate more than any other important variables. Variations in water as they affect the concentration of the soil solution are obviously also a factor affecting pH. The data presented indicate, however, that at dilutions ranging between field moisture and 10 parts of water to 1 of soil, the effect of variation in water is comparatively small at constant  $\text{CO}_2$  pressures. It therefore appears that the major effect of changing the soil-water ratio in pH determinations, using water relatively free from  $\text{CO}_2$ , is due to a dilution of the  $\text{CO}_2$  adsorbed by the soil samples. Figures 3 and 4 show that in the presence of an excess of solid phase the amount of water did not appreciably affect the pH of  $\text{CaCO}_3$  or  $\text{MgCO}_3$  in water at constant  $\text{CO}_2$  pressure. In soils (fig. 2) a slight reduction in pH resulting from dilution at constant  $\text{CO}_2$  pressure was observed, indicating that the systems were not quite comparable to pure systems of calcium and magnesium carbonates, a result which was to be expected because of the mixture of other crystalloidal and colloidal salts. The reduction of pH due to dilution, however, was comparatively small with  $\text{CO}_2$  constant, and the dilution effect evidently was less pronounced as dilution decreased.

Since pH is a variable function, any single determination can be regarded only as a point on a curve rather than a constant property of the soil. Unless the coordinates of the point are known, therefore, any single pH value has little real meaning. If, as the data seem to indicate, the effect of variations in  $\text{CO}_2$  is large in comparison with the effect of variations of other factors, then an expression or a curve showing the change in pH with  $\text{CO}_2$  should approximately show the changes under field conditions with changes in  $\text{CO}_2$  pressure. If it is assumed that the  $\text{CO}_2$  pressure might vary between the limits of the  $\text{CO}_2$  pressure in the air above the soil and an atmosphere at local points adjacent to the plant roots, a curve showing the effect of  $\text{CO}_2$  pressure on pH between these limits should be of value in classifying the soil with respect to the properties affected by soil reaction. Below 1 atmosphere of  $\text{CO}_2$ , which is the maximum that could occur in the field, pH was found to be approximately a straight-line function of the log of the  $\text{CO}_2$  pressure at constant moisture. It is therefore suggested that instead of expressing pH of soil as a single value determined under standard conditions, a better procedure for many purposes would be to determine two points at known  $\text{CO}_2$  pressures and express pH in the form of an equation or graphically as a curve. For example, the equation showing the pH change with  $\text{CO}_2$  pressure at 1 part soil to 2 parts water for soil 1 (tables 1 and 2) would be  $\text{pH} = -.752 \log \text{CO}_2 + 6.318$ , when  $\text{CO}_2$  is expressed in atmospheres. If the pH under an unknown  $\text{CO}_2$  pressure is determined, the equation also furnishes a method of calculating the  $\text{CO}_2$  pressure.

There is also the possibility of expressing pH as a function of the amount of  $\text{CO}_2$  added to the soil system rather than as a function of the  $\text{CO}_2$  pressure. Because of reactions with the soil, the  $\text{CO}_2$  pressure is not necessarily proportional to the amount added. A study of the effect of the amount of  $\text{CO}_2$  added upon pH is being made.



Determinations of pH in a suspension of soil in distilled water with a very low  $\text{CO}_2$  content, because the soil is under a lower  $\text{CO}_2$  pressure than is ever found in the field, probably would give a much higher pH for calcareous soils than is ever found in the field. For this reason, single pH determinations made under such conditions are limited in usefulness. It is suggested that, for single-value pH determinations, equilibrating the soil with air before the determination would give a better value because such a value would approximate the maximum pH of the soil under field conditions. Another pH value obtained by equilibrating the sample with a stream of pure  $\text{CO}_2$  gas would give the approximate minimum pH value for field conditions. Connecting the two points would give a curve characteristic of the soil.

#### SUMMARY

A study of the pH of soils as a function of  $\text{CO}_2$  pressure and moisture percentage has brought out the following facts:

Small changes in  $\text{CO}_2$  pressure cause comparatively large changes in pH within the range of low  $\text{CO}_2$  pressures comparable to those normally found in the soil.

The pH is approximately a straight-line function of the log of the  $\text{CO}_2$  pressure in the pressure range from about 0.0003 to 1 atmosphere of  $\text{CO}_2$  at constant moisture.

At constant  $\text{CO}_2$  pressure the pH of soil suspensions tends to drop slightly with dilution.

The rise in pH of soils frequently observed with increasing water content probably is due primarily to dilution of the  $\text{CO}_2$  absorbed in the soil sample.

The curves showing the effect of variations in  $\text{CO}_2$  pressure on pH of the soils studied were similar in shape to curves for  $\text{CaCO}_3$  but were affected more by dilution than were the curves for calcium or magnesium carbonate.

Curve positions are changed appreciably on the pH scale by the presence of calcium, magnesium, or sodium carbonates. The curves tend to group themselves into families depending upon the presence or the absence of one or more of these compounds.

It is concluded that expressing the pH of soils as variable functions of  $\text{CO}_2$  pressure would give a better indication of the probable pH range in the field in the presence of plant roots and decaying organic matter than could be obtained from single pH measurements. Since the pH is apparently a straight-line function of the log of the  $\text{CO}_2$  pressure, two points would be sufficient to determine a curve at constant moisture. Whether single determinations or curves are to be used in expressing pH values, it is evidently necessary to make measurements under equilibrium conditions with controlled  $\text{CO}_2$  pressure if the results are to be reproducible. Controlling  $\text{CO}_2$  pressure by using distilled water treated to remove  $\text{CO}_2$  in making pH determinations has the disadvantage of producing a  $\text{CO}_2$  pressure lower than would likely be found in the field and, therefore, giving pH values higher than the maximum under field conditions.

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# THE IMPORTANCE OF AGITATION OF THE SOIL SUSPENSION WITH THE GLASS ELECTRODE

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It has been long established that agitation of the soil suspension is essential with the hydrogen electrode (1, 2, 3, 5, 6, 7, 8). In the use of the glass electrode it has usually been assumed that agitation is not necessary. Soil suspensions are merely shaken and poured into the electrode vessel for measurement. This assumption is based on the fact that the glass electrode is more sensitive and comes to equilibrium much sooner than the hydrogen electrode. The author is aware of no experimental tests heretofore on this subject. The purpose of this paper is to present data showing the effect of agitation of the soil suspension when pH values are measured with the glass electrode.

## MATERIALS AND METHODS

Hydrogen-ion determinations were made on 13 soil profiles, consisting of 57 horizon samples, with both the bubbling hydrogen electrode described in a previous publication (1) and a quinhydrone glass electrode (4). Though this latter type of electrode is now replaced by a permanently sealed glass electrode containing silver, silver chloride, or other suitable materials, the necessity for agitation of soil suspensions is in no way altered. The soils used were from New Jersey and from California and ranged in texture from sand to heavy clay. With both methods air-dried soils were used. A soil-water ratio of 1 part of soil to 2 parts of distilled water by volume, the most commonly used with the hydrogen electrode, was employed. Both the hydrogen electrode and the glass electrode were lowered as deeply as possible into the soil suspension without danger of breakage from pressure against the bottom of the electrode vessel.

At first, some of the results obtained by the two methods showed considerable disagreement. This was true especially of the lighter textured samples when the soil suspension with the glass electrode was merely shaken but not agitated during the reading. In several instances the drift of the potentiometer was so rapid that it was difficult to read. Compressed air was then used to agitate the soil suspension in the vessel containing the glass electrode. The air was purified by running it through a concentrated solution of NaOH to remove the  $\text{CO}_2$ , then through a saturated  $\text{H}_3\text{BO}_3$  solution to remove  $\text{NH}_3$ , and then through distilled water to remove the  $\text{H}_3\text{BO}_3$  that might be carried over as spray. The vessel used was similar to that employed with the bubbling hydrogen electrode.

## DISCUSSION OF RESULTS

Table 1 gives the results obtained by the bubbling hydrogen electrode method and by the glass electrode with and without agitation. The agreement between the bubbling hydrogen electrode method and the compressed air agitated glass

TABLE 1

*Comparison of pH values of soils determined with the hydrogen electrode and with the glass electrode and the effect of agitation on the glass electrode results*

SAMPLE NO.	SOIL TYPE	DEPTH	HYDROGEN ELECTRODE AGITATED	GLASS ELECTRODE	
				Agitated	Non- agitated
		<i>inches</i>	<i>pH</i>	<i>pH</i>	<i>pH</i>
C-991	Gloucester sandy loam*	0-3	4.10	4.10	4.50
92		3-9	4.29	4.29	4.77
93		9-20	4.49	4.49	5.12
94		20-30	4.63	4.63	5.17
95		30-50	5.10	5.10	5.27
96		50-60	5.15	5.15	5.47
5786103	San Joaquin loam†	0-16	6.59	6.63	6.69
104		16-24	8.10	8.10	8.29
105		24-34	7.92	7.92	8.20
106		34-66	8.23	8.23	8.65
5786183	Greenfield sandy loam†	0-12	7.03	6.97	7.25
184		12-40	7.37	7.37	7.83
185		40-55	7.47	7.42	8.00
186		55-70	7.50	7.50	7.93
5786142	Ducor clay†	0-12	8.13	8.09	8.09
143		12-22	8.13	8.16	8.16
144		22-34	8.27	8.27	8.27
145		34-46	8.29	8.29	8.43
146		46-60	8.53	8.53	8.79
5786107	San Joaquin clay loam†	0-14	7.00	7.00	7.12
108		14-21	7.25	7.25	7.50
109		21-30	7.39	7.39	8.02
110		30-34	8.15	8.19	8.49
111		34-54	8.27	8.27	8.85
112		54-62	8.43	8.43	8.75
578421	Sacramento clay adobe†	0-10	5.98	6.00	6.00
22		10-45	6.39	6.40	6.40
23		45-72	8.00	8.10	8.17
578404	Oakley sand†	0-12	6.32	6.32	6.32
05		12-47	6.15	6.23	6.23
06		47-72	6.25	6.27	6.27
578428	Marsh Creek clay loam†	0-10	6.60	6.55	6.55
29		10-44	6.96	7.00	7.00
30		44-72	8.12	8.20	8.29
578459	Lamora loam†	0-12	7.08	7.13	8.27
60		12-40	6.27	6.27	6.27
61		40-72	6.52	6.49	6.49

TABLE 1—(Concluded)

SAMPLE NO.	SOIL TYPE	DEPTH	HYDROGEN ELECTRODE AGITATED	GLASS ELECTRODE	
				Agitated	Non- agitated
		<i>inches</i>	<i>pH</i>	<i>pH</i>	<i>pH</i>
578586	Kaweah clay§	0-8	6.94	6.93	7.02
87		8-24	7.29	7.25	7.30
88		24-28	7.35	7.35	7.42
89		28-34	8.20	8.20	8.32
90		34-58	8.35	8.29	8.43
578533	San Joaquin loam§	0-10	6.33	6.35	6.40
34		10-20	6.43	6.43	6.70
35		20-38	7.62	7.62	7.92
36		38-72	7.29	7.25	7.42
578565	Fresno fine sandy loam§	0-9	9.73	9.73	9.90
66		9-20	10.20	10.20	10.33
67		20-30	9.49	9.50	9.59
68		30-38	9.25	9.30	9.42
69		38-48	9.03	9.07	9.22
578518	San Joaquin clay loam§	0-9	6.25	6.32	7.17
19		9-19	6.59	6.60	6.89
20		19-27	6.98	7.00	7.17
21		27-30	7.75	7.83	8.07
22		30-40	8.02	8.02	8.23
23		40-80	7.63	7.57	7.62

\* From Morris County, New Jersey.

† From Pixley area, California.

‡ From Contra Costa area, California.

§ From Visalia area, California.

electrode method is very close: the results check with every sample to within 0.1 pH. The results obtained by the glass electrode with and without agitation differ much more widely: of the 57 samples, 36 show a value more than 0.1 pH higher when the soil suspension was not agitated during the reading than when the soil suspension was agitated; 7, a value more than 0.5 pH higher; and 1, a value 1.14 pH higher.

In general, agreement between the agitated and the nonagitated soil suspensions is very good for the clays high in colloidal content but poor for the coarser textured soils low in colloids. There are, however, several notable exceptions; namely, perfect agreement for the Oakley sand profile from the Contra Costa area in California, and poor agreement for the San Joaquin clay loam profiles from the Visalia and Pixley areas, California. The sample showing the greatest divergence between agitation and nonagitation with the glass electrode is the surface 12 inches from the Lamora loam profile from the Contra Costa area, California. Of the six other samples that show differences of more than 0.5 pH, two are from clay loam profiles and four from sandy loam profiles. In every case where there is a differ-

ence between the agitated and the nonagitated suspension, the nonagitated suspension has a higher pH.

#### CONCLUSIONS

Agitation of the soil suspension with the glass electrode is essential for reliable results, especially with coarse-textured soils, the particles of which settle out quickly. The tendency is to obtain the pH of the soil extract rather than that of the soil suspension when agitation is not employed. The heavy soils, high in colloidal content, tend to show less differences between agitation and nonagitation, because colloids stay in suspension for a relatively long time. There are too many exceptions to this rule, however, to warrant relying on nonagitation for heavy soils. The purpose of agitation is to bring the nonsuspended soil particles, as well as the suspended and soluble portions of the soil, into direct contact with the electrode so as to obtain the true hydrogen-ion concentration of the soil suspension.

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# EXCHANGEABLE CATION STATUS AND STRUCTURE OF PALOUSE SILTY CLAY LOAM AS INFLUENCED BY VARIOUS CROPPING AND FERTILITY PRACTICES<sup>1</sup>

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Under the influence of certain chemical and physical forces, discrete soil particles aggregate to form definite units characteristic of their environments. The end product of this process is soil structure. Recent investigations have shown that the physical and chemical agents responsible for the formation of structure are readily affected by various soil management practices, and these, in turn, influence the state and stability of soil structure (1, 5, 6, 9, 14). The comparative measurement of the alterations in the forces of attraction among soil particles thus provides a means for estimating the magnitude of these changes and for evaluating the structural effects of the agricultural program.

In 1921, three series of experimental plots which received different organic and inorganic fertilizers under continuous wheat and alternate wheat-fallow cropping systems were established on Palouse silty clay loam, a prairie soil found in southeastern Washington. Noticeable structural differences soon appeared in the field among the several plots, and at the end of the twentieth year it was thought opportune to measure these differences and to ascertain the factors responsible.

## PHYSICAL PROCEDURES

Structure was evaluated by measuring the water stability of the soil aggregates over a size distribution from  $\frac{1}{4}$  to 0.005 mm. on the same sample. The macroaggregate determinations were patterned after Yoder's method of wet sieving (15), and the microaggregate analyses were made with a Bouyoucos hydrometer (4).

Trial determinations with several existing wet-sieving procedures proved to be unsatisfactory, for no method gave consistent replicate agreements within 10 per cent. In this connection it is important to note that of the many published reports on the wet-sieving procedure only one, that by Stauffer *et al.* (14) indicates the magnitude of the replicate agreement. In this work a duplicate agreement within 10 per cent of the average of the two, equivalent to a 20 per cent variation, was regarded as adequate.

<sup>1</sup> Published as Scientific Paper No. 538, College of Agriculture and Agricultural Experiment Station, State College of Washington. The data in this paper are taken from a thesis submitted by the senior author in partial fulfillment of the requirements for the degree of master of science.

<sup>2</sup> Former graduate assistant and assistant professor in soils, respectively. The senior author is at present junior soil surveyor, U. S. Department of Interior, Soil and Moisture Conservation Operation, Indian Service. Acknowledgment is gratefully made by the authors to S. C. Vandecaveye for his suggestion of the problem and for his valuable advice and assistance in the study reported.



Critical points noted during the course of extensive preliminary studies were method of taking sample in field; transportation of sample to laboratory; selection of aggregates to be analyzed, especially with reference to material of a definite size range; moisture content of soil at time of analysis; method of weighing sample and placing it in the sieve nest; and free movement of water through the nest during the oscillation period.

Field samples were taken with a sampling core designed in accordance with the suggestions of Nichols (11) to minimize compression. All of the analyses were made in the range of moisture content of 19 to 24 per cent, for determinations outside this range were found to increase replicate variation. To ensure complete freedom of water movement through the nest during the oscillation

TABLE 1  
*Treatments of experimental plots established on Palouse silty clay loam*

PLOT	TREATMENT	
		<i>lbs./A.</i>
99, 199	Check	
100, 200	{ Wheat straw	2,700
	{ Sodium nitrate	370
101, 201	Alfalfa hay	2,700
102, 202	{ Wheat straw	1,350
	{ Alfalfa hay	1,350
103, 203	Wheat straw	2,700
104, 204	Check	
105, 205	{ Wheat straw	2,700
	{ Sodium nitrate	370
106, 206	Sodium nitrate	370
107, 207	{ Wheat straw	2,700
	{ Ammonium sulfate	286
108, 208	Farm manure	12,000

period, a 100-mesh sieve used by many investigators was replaced by a spillway sieve, suggested by Elson (5).

No particular analytical difficulties were experienced with the microaggregate determinations, which were run on the moist soil material not used in the macroaggregate analyses.

Field samples were taken in the spring of 1941 before plowing, and the analyses were run over a period of 5 months. No appreciable variation in moisture content of the stored samples occurred during this time. The effect of storage on aggregation was not significant, as revealed by analyses of samples from the same plot made at the beginning and at the end of the period. Time of standing has been shown to have some effect on soil aggregation through microbial activity, but this has been demonstrated only with material lacking a definitely established structure (10).

The method finally worked out to give replicate agreement within 5 per cent was as follows:

*Macroaggregate analysis:*

Each plot was sampled in duplicate at three points 25 feet apart by means of a 6-inch sampling tube 2 inches in inside diameter, but with the cutting edge swaged to an inside diameter of  $1\frac{1}{4}$  inches.

The core samples were placed in air-tight Mason jars and transported to the laboratory.

Immediately prior to analysis, moisture samples of the soil were taken and the moist soil was sieved. Aggregates of the size distribution 1.5 to 1.0 cm. were used.

After quartering, 50 gm. of these moist aggregates were weighed directly into the 4-mm. sieve, while it was suspended from the balance beam by means of battery clamps and string. Thus if any aggregate breakdown occurred as a result of handling, the fine material was not included in the sample.

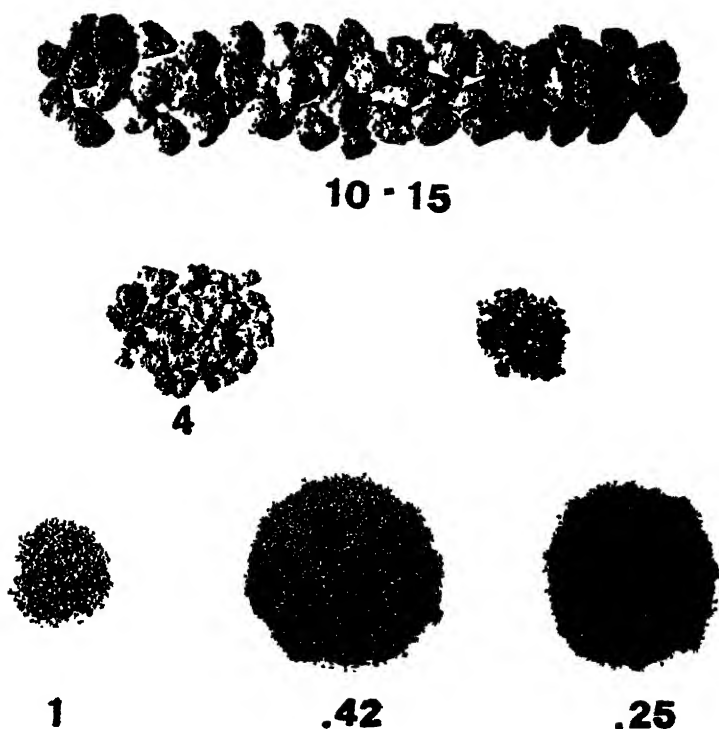


FIG. 1. NATURE OF AGGREGATES (10-15-MM. GROUP) EMPLOYED IN WET-SIEVING PROCEDURE AND TYPICAL DISTRIBUTION AND NATURE OF AGGREGATES (IN MILLIMETERS) FOUND AFTER SIEVING

The 4-mm. sieve was then transferred to its proper place in the nest, which consisted of six 5-inch wire sieves arranged in the following order. 2-mm. spillway sieve, 4-mm. sieve, 2-mm. sieve, 1-mm. sieve, 0.42-mm. sieve, and 0.25-mm. sieve.

After the nest was made water-tight with rubber bands, made from tire tubing, placed over the joints between the sieves, it was fitted into position in the washing apparatus. A suitable pulley arrangement gave a displacement of 3.15 cm. and 30 vertical oscillatory movements a minute.

Tap water was then added to large cans enveloping the nest, to such a height that it barely passed over the top of the 2-mm. spillway sieve at the bottom of the down stroke, thus providing continual drainage through the nest.

The apparatus was next set in motion for 1 hour, after which the water was siphoned from the cans and the sieves were allowed to drain.

The aggregates retained by each sieve were quantitatively transferred to weighed breakers and their weight determined after oven-drying at 110°C. The apparatus enabled the running of two analyses at the same time. The nature of the aggregates obtained is shown in figure 1.

#### *Microaggregate analysis:*

The moist soil was sieved immediately prior to analysis, and the fraction 1.0 to 0.42 mm. was used.

An amount of these moist granules equivalent to 50 gm. of dry soil was placed in a hydrometer cylinder, which was then filled to proper volume and shaken end over end 20 times.

Hydrometer readings were taken at 40 seconds, 17 minutes, and 1 hour; these readings made it possible to calculate the following particle size distributions. >0.05 mm., 0.05-0.01 mm., 0.01-0.005 mm., and <0.005 mm.

All determinations were run in duplicate on the soil samples from each of the three sampling points. The data for each fraction are expressed in percentages of the original sample based on the oven-dry weight. In expressing the results, it was not considered necessary to introduce a correction factor for the unaggregated sand particles retained by the sieves, since 95 per cent of the total sand of the samples is very fine (0.25 to 0.10 mm.) and could not be retained in an unaggregated state by any of the sieves employed.

Mechanical analyses were made on all the check plots with a Bouyoucos hydrometer to see whether any appreciable variation in texture existed.

#### CHEMICAL PROCEDURES

Alterations in the cation exchange status of the various plots were investigated on composite samples made from the soil material taken at the three sampling points. The samples were thoroughly mixed, air-dried, and stored in sealed containers. The exchangeable bases were extracted with  $(\text{CH}_3\text{COO})\text{NH}_4$  and the organic matter was destroyed by  $\text{HClO}_4$  and  $\text{HNO}_3$  treatments. Calcium was determined volumetrically after precipitation as the oxalate; magnesium, volumetrically after precipitation as  $\text{MgNH}_4\text{PO}_4$ ; sodium, gravimetrically as sodium uranyl acetate; and potassium, volumetrically after precipitation as the cobaltinitrate.

Exchangeable hydrogen was determined by the  $(\text{CH}_3\text{COO})_2\text{Ba}$  method of Parker (12) with slight modifications. Total exchange capacity was calculated from the summation of the exchangeable cations.

The values for the organic matter contents of the various plots were calculated from the data of Holtz and Vandecaveye (7), who worked on the same plots. It was thought that the trends reported by them continued in the same direction. These analyses were made on samples taken in the fall of 1934. For the conversion of their carbon values to percentage organic matter, the standard factor 1.724 was used.

## RESULTS

The results of the mechanical analyses of the check plots, presented in table 2, reveal a slight textural variation among the plots. This is, no doubt, caused by a ridge running along plots 99 and 199; in the loessial soils of southeastern Washington, such ridges are commonly higher in clay content than is the level soil.

The macroaggregate and microaggregate determinations are presented in tables 3 and 4 as plot averages from which extreme values and variations due

TABLE 2  
*Mechanical analysis of check plot soils*

PLOT	SAND	SILT	CLAY
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
99	19.2	55.6	25.2
104	21.2	55.2	23.6
199	19.2	53.2	27.6
204	23.2	53.2	23.6

TABLE 3  
*Aggregate analysis of soil from continuous wheat plots of the 100 series\**

PLOT	MACROAGGREGATES						MICROAGGREGATES			
	>4.0 mm.	2.0 mm.	1.0 mm.	0.42 mm.	0.25 mm.	<0.25 mm.	>0.05 mm.	0.01 mm.	0.005 mm.	<0.005 mm.
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
99	11.9	6.9	5.8	23.8	12.7	38.9	64.0	24.0	4.3	7.7
100	52.0	6.4	3.5	11.8	5.2	21.1	54.0	28.8	7.2	10.0
101	17.3	5.1	3.6	24.7	13.5	35.8	67.2	23.4	3.3	6.1
102	27.0	5.1	3.2	18.6	12.2	33.9	64.9	24.7	2.8	7.6
103	52.7	3.8	1.6	10.8	7.7	23.4	64.4	23.6	4.7	7.3
104	12.6	5.1	3.9	25.9	12.6	39.9	62.7	25.6	4.1	7.6
105	31.0	4.8	3.4	18.9	10.2	31.7	60.9	26.0	3.9	9.2
106	11.0	6.2	4.0	25.8	12.3	40.7	57.7	28.7	4.0	9.6
107	31.8	4.2	2.5	13.8	10.7	37.0	60.3	26.7	2.7	10.4
108	70.9	2.9	1.3	3.5	5.0	16.4	65.3	24.1	4.1	6.4

\* Plot averages from which extreme values and variations due to natural soil heterogeneity have been eliminated.

to natural soil heterogeneity have been eliminated. Out of a total of 720 macroaggregate fractions determined, only 15, or 2.08 per cent, failed to agree with their replicates within 5 per cent. In such cases the single value most closely approaching the other data from the same plot was selected. Variations due to natural structural heterogeneity were found to exist in 16 determinations, or 1.33 per cent, of a total of 1200 macroaggregate and microaggregate fractions. These values remained out of line during redeterminations that agreed within 5 per cent.

The results show a wide variation in the water stability of the macroaggregates among the plots, the significance of which will be discussed later.

For the microaggregates, the differences tended to disappear. This is to be expected in view of the fact that the closer the material approached its ultimate textural classification, the smaller would the variation among the plots become, since these all belong to the same soil type.

The exchange status and the organic matter contents of the various plots are presented in table 5. The use of ammonium sulfate has lowered the degree of base saturation of the exchange complex as indicated by the higher exchangeable hydrogen content of the plots so treated. This effect was especially marked in plot 107 of the continuous wheat series, the unsaturation in this plot being 29.7 per cent as compared to an average of 19.6 per cent for all of the plots of the continuous wheat series.

TABLE 4  
*Aggregate analysis of soil from alternate wheat plots of the 200 series\**

PLOT	MACROAGGREGATES						MICROAGGREGATES			
	>4.0 mm.	2.0 mm.	1.0 mm.	0.42 mm	0.25 mm.	<0.25 mm	>0.05 mm.	0.01 mm	0.005 mm	<0.005 mm.
	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
199	21.0	6.2	5.1	24.1	9.7	34.2	58.5	25.1	6.0	10.3
200	41.1	6.3	3.8	14.6	5.3	28.9	57.4	25.1	6.4	11.1
201	57.5	3.0	2.0	9.0	5.5	13.0	52.8	29.8	7.7	9.9
202	59.3	3.5	2.7	10.3	6.1	19.0	57.8	27.2	5.6	9.4
203	79.3	1.8	1.2	5.2	3.5	9.0	60.8	26.3	4.3	9.5
204	33.8	6.1	4.1	17.7	8.5	36.5	55.8	28.0	6.0	12.5
205	49.1	3.4	2.3	10.4	5.6	23.1	57.5	27.1	4.7	11.3
206	40.5	4.1	3.1	12.3	7.7	32.3	46.9	28.0	9.3	15.7
107	44.4	5.1	2.9	14.5	9.0	24.1	53.6	26.0	8.7	11.7
208	73.7	2.3	1.3	5.7	3.8	13.3	55.6	26.0	8.0	10.4

\* Plot averages from which extreme values and variations due to natural soil heterogeneity have been eliminated.

The complex is dominated by calcium, which satisfied approximately 50 per cent of the exchange capacity. The use of ammonium sulfate has caused a loss of calcium. Replaceable magnesium showed no appreciable variation either within or between the two series.

The application of sodium nitrate in every case increased the content of exchangeable sodium, the greatest increase being shown by the early spring application in the 100 series. The exchange complex of the soil material of plot 100 was about 8 per cent sodium-saturated. This corresponds to a retention by the surface soil of 1.35 m.e. per 100 gm., or 35 per cent of the applied sodium, since about 4 m.e. of sodium was added to each 100 gm. of soil over the 20-year period.

The exchangeable potassium showed greater variation within the series than between them. The heavier textured plots along the ridge showed the lowest replaceable potassium.

The average total exchange capacity of the continuously cropped plots was 1.16 m.e. higher than that of the alternately cropped plots. This correlates

with the higher organic matter content of the former, and it is significant to note in the average values that the additional exchange positions are approximately equivalent to the increment of exchangeable hydrogen.

The percentage organic matter, as calculated from the data of Holtz and Vandecaveye (7), was significantly higher for the continuous than for the summer-fallow farming system. This is due to the greater quantity of organic amendments which the former received as well as to the possible repression of

TABLE 5

*Cation exchange status and organic matter content of soil from experimental plots*

PLOT	EXCHANGEABLE CATIONS						ORGANIC MATTER†
	H	Ca	Mg	Na	K	Total	
	m.e.*	m.e.*	m.e.*	m.e.*	m.e.*	m.e.*	per cent
99	5.13	12.88	4.55	0.59	0.63	23.78	....
100	3.63	11.80	4.64	1.94	0.66	22.67	3.24
101	4.30	12.30	4.60	0.58	0.98	22.76	3.45
102	4.18	13.60	4.70	0.57	1.08	24.13	3.38
103	3.85	13.30	4.62	0.72	1.44	23.93	3.28
104	4.80	12.30	4.20	0.59	1.09	23.98	3.10
105	2.90	11.35	4.20	1.27	1.54	21.26	3.43
106	4.75	11.08	3.89	1.02	0.90	21.64	3.42
107	6.75	10.25	3.64	0.75	1.34	22.73	3.70
108	4.95	12.20	4.60	0.98	2.05	24.78	4.19
Average...	4.52	12.11	4.36	0.90	1.17	23.06	3.47
199	3.50	14.05	4.64	0.71	0.65	23.55	....
200	2.65	13.40	4.59	1.00	0.88	22.52	2.93
201	3.15	13.30	4.90	0.73	1.07	23.15	3.00
202	3.45	12.75	4.95	0.71	1.14	23.00	2.98
203	3.25	12.00	3.84	0.74	1.66	21.49	3.07
204	3.15	11.50	4.40	0.71	1.10	20.86	3.00
205	3.25	11.30	4.48	0.92	1.24	21.19	3.07
206	3.83	11.20	3.35	0.98	1.19	20.55	3.07
207	3.90	10.60	4.90	0.82	1.22	21.44	3.14
208	3.58	11.40	3.90	0.87	1.46	21.21	3.25
Average...	3.37	12.15	4.40	0.82	1.16	21.90	3.06

\* Per 100 gm. soil.

† Calculated from data of Holtz and Vandecaveye (7).

microbial activity, caused by the absence of an optimum moisture regime in the surface soil at a time when the temperature regime is favorable. The manured plots are highest in organic matter and it is to be noted that the use of nitrogen fertilizers or nitrogen-containing organic materials tended to conserve the soil humus. This effect was more striking for the 100 series than for the 200 series, probably because humus decomposition during the fallow period exceeded its formation during the 2-year cycle.

## DISCUSSION

A comparison of the two cropping systems reveals that the stability of the macroaggregates is greater for the 200 series than for the 100 series, but for the microaggregates the reverse is true. This fact would seem to indicate that a different set of forces is responsible for the stability of each type of aggregate.

Though the reasons for the difference between the macroaggregate stability of the two series are obscure, several possible causes may be indicated. First, the 200 series was in crop the previous summer and had not been plowed for summer-fallowing at sampling time. The 100 series, on the other hand, had been plowed, seeded to fall wheat, and was supporting a crop. The cropping practice immediately prior to sampling undoubtedly affects structure, although it is difficult to evaluate the effect quantitatively. Second, differences in the character of the tillage operations under the two cropping systems may have exerted a strong influence. Though the operations may be more numerous for the alternate series, they are more superficial in character. The number of deep plowing operations is greater for the continuously cropped plots. Third, the summer-fallow period in the 200 series provides ample opportunity for the building of a stable macrostructure under a moisture regime that is favorable for aggregate formation by microbial activity. Fourth, the difference in root activity under each system may exert a strong influence. No attempt has been made to evaluate the precise effect of each of these factors on the soil material of the two plot series.

The data also indicate that the fortification of straw with nitrogen fertilizers or with organic residues high in nitrogen causes a decline in macroaggregate stability. This tendency is most pronounced in the 100 series. Plots that received straw residues supplemented with  $\text{NaNO}_3$  or  $(\text{NH}_4)_2\text{SO}_4$  revealed less stability than those receiving straw alone. Those receiving straw plus alfalfa hay showed greater stability than those receiving alfalfa hay alone but less stability than those receiving straw alone. All plots that received organic material were more stable than the checks. Applications of  $\text{NaNO}_3$  alone resulted in a decrease in stability to a value below that of the checks.

The findings of Holtz and Vandecaveye (7), who worked on the same plots, showed that the formation of soil humus is dependent upon the amount of nitrogen in the residue. It is also possible that the presence of an ample supply of nitrogen may hasten the process of organic matter transformation, regardless of whether the organic matter is dissipated as  $\text{CO}_2$  or is retained by the soil as humus. If this is so, then addition of nitrogen to the strawy residue should result in a decrease in the amount of straw fragments and hence a decrease in the mechanical binding of which the straw fragments might be capable. Clods taken from the various plots of the continuous wheat series (fig. 2) tend to support this explanation.

In the alternate cropping system, the effect of nitrogen amendments is masked by other processes inherent in that system. During the fallow period sufficient nitrogen is made available by microbial activity to take care of the needs of the microorganisms and the growing wheat. Hence the quantities of straw frag-

ments that persist in the soil are relatively small and to a great extent independent of the nature of the organic and inorganic treatments. The result is that although the level of macroaggregate stability in the 200 series is higher than that in the 100 series, the principle of the relation between the sufficiency of the nitrogen supply and the aggregating power of straw is inapplicable.

No connection was discernible between the exchangeable cations and the macrostructure.

The microaggregates respond more directly than the macroaggregates to the physicochemical colloidal effects of the treatments. The greater water stability of the microaggregates in the 100 series is readily explained on the basis of the significantly higher organic matter content of the soil under this cropping system, resulting from the greater quantities of organic residues received. The

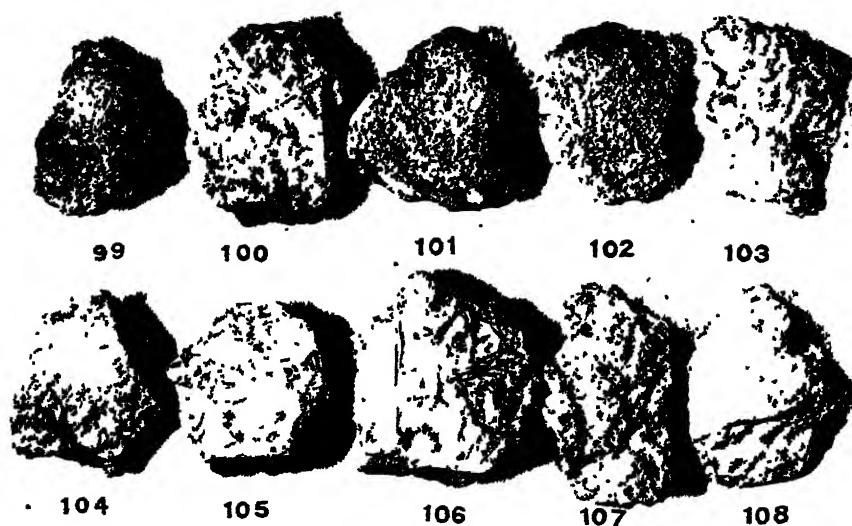


FIG. 2. APPEARANCE OF CLODS TAKEN FROM PLOTS OF THE 100 SERIES

importance of organic matter in maintaining the stability of soil aggregates has been pointed out by other investigators (1, 5, 6, 13).

When the supplemental source of nitrogen is inorganic, complicating cationic relationships become involved in the microaggregate instability.

If the percentage of material in the fraction less than 0.005 mm. is used as an index of microaggregate instability, the average value of the plots receiving inorganic nitrogen materials alone or as a supplement was 11.1 per cent, that of the check plots was 9.5 per cent, and that of the plots receiving organic residues alone was 8.3 per cent.

In the absence of investigations on the colloidal behavior of Palouse silty clay loam under controlled cation conditions, it is difficult to explain the dispersive action of  $(\text{NH}_4)_2\text{SO}_4$ . However, the increase in exchangeable hydrogen of the plots receiving  $(\text{NH}_4)_2\text{SO}_4$  occurred largely at the expense of calcium, and there



is some evidence from studies under regulated cation environments that calcium may exert a stronger flocculating power than hydrogen (2, 3). Thus it may be possible by the continued use of a physiologically acid fertilizer to cause less favorable structural conditions if the exchange complex primarily suffers a loss of its calcium in becoming more unsaturated.

The adverse structural effects of the highly hydrated sodium ion, when it is present in the clay complex, is well known. Mattson (8) has shown that when

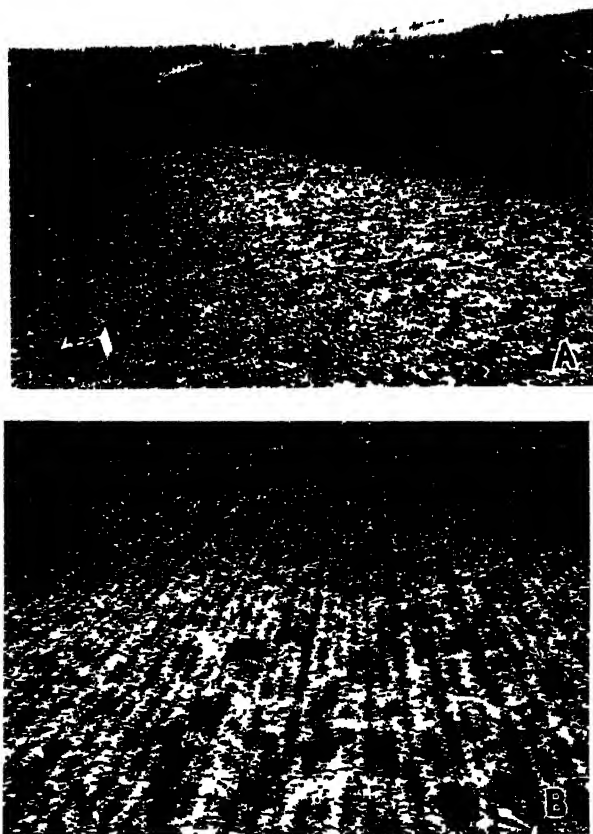


FIG. 3. APPEARANCE OF FIELD PLOTS OF THE 100 SERIES

A (top): left, plot 99; right, plot 100

B (bottom). background, plot 107, foreground, plot 106

approximately 25 per cent of the exchange positions are occupied by Na in a mixed Na-Ca-system, the colloid assumes appreciably the hydration and swelling characteristics of a Na-system. Since the maximum degree of Na-saturation found in the present study was only 8 per cent, the influence of the Na ion might not be expected to be very strongly expressed. Actually, the puddled appearance of the plots in the field indicated that this relatively small degree of Na saturation had modified the physical condition of the soil to a noticeable degree. This effect is shown in figure 3, where the plots receiving  $\text{NaNO}_3$  appear

as light-colored areas, because of the more highly reflecting nature of the puddled surface film of soil material. The skinlike character of this surface is apparent on clods 100, 105, and 106 in figure 2, where one may also see the vesicular character of the material immediately underlying the puddled surface. Undoubtedly, the impact of rains has been responsible for this puddling, but in the present state of Na saturation the puddling action is not transmitted to the underlying material. As a consequence, the striking physical appearance in the field, being only superficial in character, was not fully reflected in the physical analyses in the laboratory, since the latter were carried out with samples taken to a depth of 6 inches.

Further experiments are being planned to investigate the puddling attributes and the effect of the present condition of the plots upon infiltration rates. Yield data indicate a stronger tendency for "burning" to occur on the plots receiving inorganic nitrogen applications annually. It is possible, if infiltration rates are lower on these plots, that the tendency of the nitrogen to cause "burning" is being accentuated by a lower moisture content.

#### SUMMARY

An investigation was conducted into the effect of various cropping and fertility practices on the structure and exchange status of Palouse silty clay loam. Structure was evaluated by measuring the water stability of the aggregates, a wet-sieving procedure being used for the macroaggregates, and the Bouyoucos hydrometer for the microaggregates.

The data indicate that mechanical forces dominate the formation of the larger aggregates, whereas physicochemical colloidal reactions govern the smaller granules. Plots cropped annually to wheat were found to possess a less stable macrostructure than those alternately cropped and fallowed. The microstructure of the annually cropped plots, however, appeared to be more stable as a result of the presence of more organic colloid.

Additions of straw and manure resulted in greatest macrostability; alfalfa hay and straw supplemented with nitrogen, in less; and the check plots and the plots receiving  $\text{NaNO}_3$  alone, in the least. Microstructure was adversely affected when the nitrogen was supplied as  $\text{NaNO}_3$  or  $(\text{NH}_4)_2\text{SO}_4$ .

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# A METHOD FOR MEASURING THE PLANT RESIDUE FRAGMENTS OF THE SOIL

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The recent work of Duley and Russel (2, 4, 11) has emphasized the importance of plant residues left at the surface for soil and water conservation. The residues retained on the surface of the soil dissipate the energy of the falling rain-drops, prevent the rapid formation of compact surface layers, retard runoff, permit maximum water intake (3), and reduce evaporation and soil erosion. The degree to which residues bring about these effects is related to the amount, kind, and possibly the state of decomposition of the residues at the surface of the soil. In order to evaluate the protection the soil is receiving from residues at any specified time, it is important to know the amount of plant materials left on the surface of the soil.

Plant materials are composed of a variety of chemical complexes susceptible to attack by microorganisms which use these substances as sources of energy and for the synthesis of microbial tissue. Upon contact of the plant residue with the soil, under favorable weather and soil conditions, decomposition of the organic material by the microorganisms begins. The original quantity of plant materials exists for only a brief period after the materials are applied to or left in place on the land.

The amount of residue remaining at any time is inversely related to the microbial activity, which in turn is governed to a large degree by the extent of surface area contact between the soil and the residue and by the resistance to microbial enzymes of the undecomposed portion because of its chemical nature.

Organic matter studies in the past have been largely confined to the estimation of humus in terms of carbon, nitrogen, or oxidizable materials (14). The decayed substance, however, does not give the same type of protection to the soil as does the undecomposed plant material.

In the Great Plains region the humus content of the surface soil may constitute 4 per cent or more, which would be about 40 tons per acre. The amount of wheat straw returned to the soil by general farming practices, where combines are used, varies from about 1 to 3 tons per acre. This raw organic matter at the time of addition constitutes only approximately 5 per cent of the total organic substances in the soil. These amounts are hardly measurable by the routine methods of analysis.

<sup>1</sup> Cooperative agent (associate bacteriologist), senior soil conservationist, and professor of agronomy, respectively.

<sup>2</sup> Contribution from the Soil Conservation Service, U. S. Department of Agriculture, and the Department of Agronomy, Nebraska Agricultural Experiment Station. Journal Series No. 307.

## HISTORICAL

Some investigators have attempted to determine the undecomposed plant material of the soil by chemical means. Robinson and Jones (10) and Jones (7) used 6 per cent  $H_2O_2$  as an oxidizing agent to determine the degree of humification of plant residues and manures, the assumption being that the weak  $H_2O_2$  will oxidize only the humified material. McLean (8) considered the method unsatisfactory, because he found that the  $H_2O_2$  also attacked some of the "structural organic matter." According to this method, in soils of varying fertility, from 50 to 90 per cent of the organic matter present was humified. Pallmann and Zobrist (9) made the separation based upon nonsolubility of undecomposed material in acetyl bromide. Sibirsky (13) used sodium hypochlorite to determine the degree of humification. The nonhumified plant material such as celluloses, hemicelluloses, resins, and waxes remained insoluble in the sodium hypochlorite.

Bouyoucos (1) determined the degree of humification by igniting at  $310^\circ$  and  $550^\circ C.$  both fresh and decomposed plant materials, and used the difference to calculate the extent of decomposition.

Other investigators have attempted a physical separation of undecomposed from decomposed plant residue. Finnell (5) attempted the measurement of raw organic matter by water flotation. A 10-gm. sample of soil was added to a test tube of water and shaken. Rings of suspended organic matter were allowed to collect on the walls of the tube as the suspension was lowered by intermittently releasing some of the water from the tube into a pan of water. The material thus collected was weighed and expressed as parts per million of soil sample. Only the material that floated was regarded as structural organic matter.

Shively and Weaver (12) used a sieving method for removing plant roots from the soil.

Harris (6) made use of liquids of different density to separate foreign materials from foods.

## METHODS

After testing different methods for the removal of undecayed organic matter from the soil, the following procedure was finally evolved for field sampling and laboratory determinations:

*Taking of samples*

The procedure of sampling should vary with conditions. Coarse residues that lie wholly on the surface were removed manually from as many as 20 areas, either circular or rectangular, and ranging in dimensions from 5 inches in diameter to 1 square yard. For determination of finer fragments and for residues that are more or less buried, the soil was sampled to two depths, 0-4 and 5-8 inches, with a brass sampling cylinder, usually of 2-inch diameter. The first depth suffices for comparisons where land has been subtilled or disked, but both depths are necessary where comparisons involve plowed land.

*Laboratory procedure*

At the laboratory any coarse material removed from the surface was first washed and rinsed free of any adhering soil on a fine sieve, then oven-dried, weighed, and computed to a pound-per-acre basis. The soil samples of each depth were composited, air-dried, and gently pulverized. The entire large sample was passed through a 3-mm. screen five times to remove the larger pieces of plant material. The debris thus removed was washed, dried at 105°C., and weighed. The organic matter recovered with this screen represented the larger pieces of material from the entire sample and could be readily identified as undecomposed plant residue.

After removal of the coarse organic material, the soil was thoroughly mixed to ensure an even distribution of organic particles, and a 20-gm. sample was put into a pint milk bottle with 250 ml. of water and 1.0 gm. of sodium oxalate. At least triplicate samples were used for each plot treatment. The bottles were placed in a horizontal shaker making 1 stroke per second for 10 minutes. A 4-inch cup with a 0.4-mm. copper screen bottom was placed in a 6-inch pan. The contents of the bottle were allowed to settle for a few seconds, and most of the liquid was decanted into the cup. More water was then added, and the contents of the bottle were washed several times in order to remove all the organic material. As the water rose in the cup and in the pan surrounding it, there was no tendency to force pieces of organic matter through the screen by the impact of the water. The cup was moved gently about in the water of the pan so that heavy particles of soil would be dislodged from the wire screen. Following this operation, the finger tip was passed lightly over the material retained on the screen in order to crush any soil aggregates and to detect the presence of small rocks or sand grains that might have been poured on the screen. The organic matter remaining was washed gently with distilled water and dried on the screen for a short time at 105°C. This material was transferred to a weighing bottle, dried at 105°C. for 12 hours, and weighed to the nearest milligram. Microscopic examination of the portion remaining in the milk bottle after several decantations showed very little or no organic matter left.

The suspension passing through the 0.4-mm. screen, which should not exceed 800 ml., was poured into a glass tube 2 inches in diameter and 2 feet in length, as shown in figure 1. A slow stream of air was passed through tube *A*<sup>3</sup> so that small bubbles passed up through the column of soil suspension. This kept the suspension agitated and tended to keep the organic matter moving toward the upper part of the liquid and to dislodge any organic matter caught by the falling soil particles. The liquid was slowly drained through tube *D* into a beaker. As the level of the liquid was lowered, the organic matter particles collected on the side of the tube by adhesion. The particles may be made to adhere more readily by adding a drop of soap solution to the surface of the liquid in the tube.

<sup>3</sup> The opening of tube *A* on the inside of the stopper was drawn out to a tip bent at a right angle and with an opening of about 1 mm. in diameter. The rubber stopper *C* was dressed on a lathe until it was cylindrical and fitted snugly in the tube.

After tube *B* was emptied, stopper *C* was removed from the tube and washed with a little water into the collecting beaker. The bottom end of the tube was also washed free of adhering soil. The organic particles adhering to the walls of the tube were washed into a clean beaker. The contents of the collecting beaker were then returned to the glass tube, and the process was repeated twice.

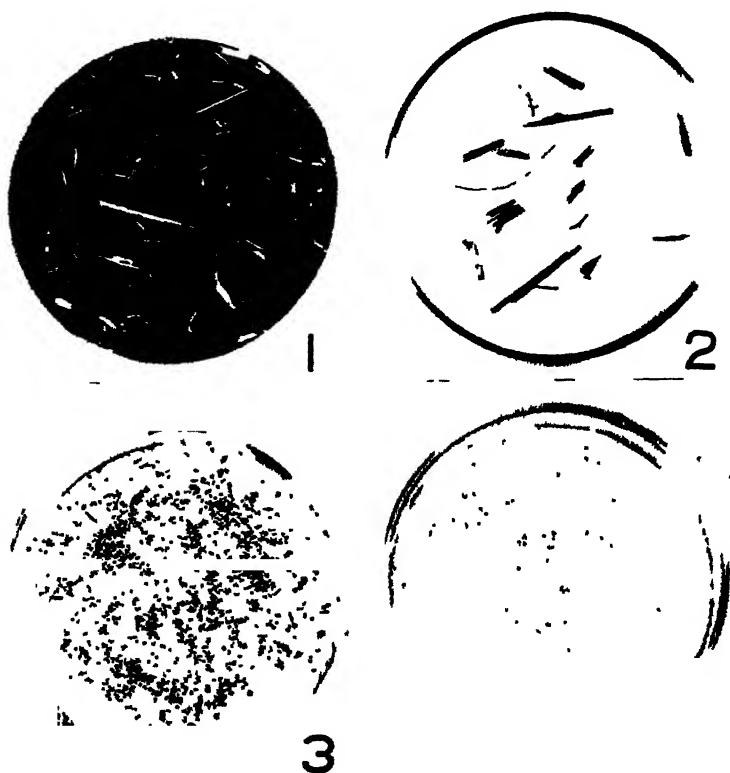


FIG. 1

FIG. 2

FIG. 1. FLOTATION APPARATUS FOR SEPARATION OF FINE ORGANIC MATTER FRAGMENTS FROM THE SOIL

FIG. 2. UNDECAYED AND SLIGHTLY DECAYED ORGANIC MATTER SEPARATES FROM 20 GM. OF SOIL

1. Original soil with plant residues. 2. Plant residues removed by dry-screening with a 3-mm. screen (42 mgm.). 3. Fraction obtained by wet-screening with a 0.4-mm. screen (67 mgm.). 4. Fine material floated out (14 mgm.).

The organic matter particles that had been washed from the walls of the tube were then transferred to a Gooch crucible with an asbestos pad, dried at 105°C., and weighed. The appearance of the three organic matter separates from a soil sample taken from a plot treated with a surface application of straw at the rate of 4 tons per acre for a 6-month period is shown in figure 2.

In some instances it may be desirable to determine only the plant residue approaching straw size. This can be accomplished by making the separation on

the dry screen. In others it may be desirable to make two or even all three size separations. This will include almost all organic matter fragments down to a size approaching that of silt.

### *Testing of method*

The variability to be expected of the method is shown by the data in table 1 with seven replicates. The material caught on the wet screen and that which was floated out and caught by adhesion to the walls of a glass tube are shown in columns 2 and 4. As indicated by the data in table 1, a variation of 5 to 10 per cent is to be expected.

Plant material of different size particles that had been removed from a field soil was added to 20 gm. of loessial subsoil devoid of plant fragments in the following concentrations: 0.1 gm. of the fraction greater than 3 mm., 0.1 gm.

TABLE 1

*Constancy of results obtained in determination of undecomposed and finely divided organic matter on a single soil\**

TRIALS	ORGANIC MATTER DETERMINED IN 20-GM. SOIL SAMPLES			
	Wet-sieved		Floated	
	<3 - >0.4 mm.	Deviation	<0.4 mm.	Deviation
	gm.	gm.	gm.	gm.
1	.062	.004	.020	.004
2	.071	.005	.017	.001
3	.065	.001	.014	.002
4	.065	.001	.015	.001
5	.073	.007	.015	.001
6	.066	.000	.017	.001
7	.060	.006	.018	.002
Mean.....	.066		.016	

\* The material larger than 3 mm. was removed from the entire field sample and weighed.

of the fraction less than 3 mm. but greater than 0.4 mm., and 0.02 gm. of the material less than 0.4 mm. These are approximately the proportions in soil under general farming conditions. Of these amounts, 99.8, 98.1, and 73.9 per cent respectively were recovered, or 96.6 per cent of the total material added, as shown in table 2. A previous determination of the water-soluble material in the straw removed showed that approximately 1 per cent of the material was leachable. With fresh straw the water-soluble material was 7.8 per cent, whereas with straw material over 1 year old this value decreased to less than 1 per cent. If straw from the outside of a stack over 1 year old and showing considerable evidence of decomposition was shaken vigorously, less than 1 per cent of the material was broken up into sizes less than 0.4 mm.

A smaller percentage of the material less than 0.4 mm. in size was separated from the soil by water flotation than by the other two screening separations. The relative proportions of these fractions, as determined 6 months after the



plots were treated with 2, 4, and 8 tons of straw per acre in the spring, are shown in table 3.

When fresh sawdust was used instead of partly decayed plant material, the recovery values were changed somewhat. Sawdust was screened dry to make size separations. When it was wetted in the screening operation, it seemed to swell, and more of the material was recovered in the upper size groups. Less sawdust than other plant material was recovered in the third fraction. The total recovery of sawdust of all fractions, however, was about the same as of

TABLE 2  
*Percentages of artificially added plant material recovered from a loessial soil*

TRIALS	SIZE RANGE OF SEPARATES			TOTAL RECOVERY OF ALL MATERIAL ADDED
	>3 mm.	<3 - >0.4 mm.	<0.4 mm.	
1	95.0	95.5	65.1	92.5
2	100.0	98.4	77.4	97.2
3	101.0	95.6	83.6	96.9
4	102.6	102.4	64.3	99.0
5	100.6	98.8	75.1	97.4
6	100.0	98.1	77.9	97.1
Mean ... ..	99.8	98.1	73.9	96.6

TABLE 3

*Amounts of straw material falling in different size groups after being on the surface of the soil for 6 months*

*Treatment and results on an acre basis*

STRAW TREATMENT	STRAW MATERIAL IN DIFFERENT SIZE GROUPS		
	>3 mm.	<3 - >0.4 mm.	<0.4 mm.
<i>tons</i>	<i>lbs.</i>	<i>lbs.</i>	<i>lbs.</i>
0	167	1357	399
2	374	2009	675
4	1013	3454	1060
8	7418	3612	807

plant material, as shown in table 4. There was 0.8 per cent water-soluble material in the sawdust used.

A series of tests was initiated to compare this method of separation with the chromic-acid and ignition methods. The plots sampled for these determinations were triplicated and the treatments were as follows: no residue, 2-ton, 4-ton, and 8-ton surface applications of straw. The amount of organic matter remaining after 6 months, as indicated by the different methods, is shown in table 5. The fraction of residue greater than 3 mm. was removed from the sample before analysis. The amounts of this coarse material found were 167, 374, 1012, and 7418 pounds per acre for no treatment, 2-ton, 4-ton, and 8-ton surface applica-

tions of straw, respectively. The results in table 5 indicate that the increases in organic material appear more consistent and reasonable by this screening and flotation method than by either the ignition or the chromic-acid method.

When this method was compared with that of Finnell (5) for removal of plant fragments from three plots receiving a previous surface application of 4 tons of straw per acre, 18 determinations gave the mean of 0.095 gm. from a 20-gm. sample by wet-screening and flotation, whereas only 0.032 gm., or about one third as much, was recovered by the method of Finnell. The individual determina-

TABLE 4

*Percentages of sawdust fractions recovered from a soil to which they had been artificially added*

TRIALS	SIZE RANGE OF SEPARATES			TOTAL RECOVERY OF ALL MATERIAL ADDED
	>3 mm.	< 3 - >0.4 mm.	<0.4 mm.	
1	102.8	102.6	36.6	96.0
2	104.2	105.8	37.5	98.6
3	105.2	104.2	31.2	98.2
4	103.3	107.2	30.6	98.6
5	100.9	105.2	43.1	99.7
6	100.3	106.2	38.3	97.3
Mean .. .	102.7	105.2	36.2	98.0

TABLE 5

*Amounts of organic matter recovered by several methods from a soil 6 months after treatment with different surface applications of straw*

*Treatment and results on an acre basis*

STRAW TREATMENT	NEW METHOD		IGNITION METHOD		READILY OXIDIZABLE	
	Residues	Increase	Loss	Increase	Loss	Increase
<i>tons</i>	<i>lbs.</i>	<i>lbs.</i>	<i>per cent</i>	<i>lbs.</i>	<i>per cent</i>	<i>lbs.</i>
0	1756		6.696		3.93	
2	2084	928	6.765	678	3.95	196
4	4496	2740	6.888	1860	4.10	1647
8	4419	2663	6.595	1091	3.96	324

tions by the method of Finnell gave very consistent values not varying over 5 per cent mean deviation.

#### SUMMARY

A procedure is described for the quantitative determination of the undecomposed or slightly decomposed part of plant residues on the surface or mixed with the soil even though broken into small bits. The plant residues were separated from the soil in three fractions: (a) The plant material greater than 3 mm. This was separated by passing the dry soil through a screen. (b) The material less than 3 mm. but greater than 0.4 mm. This fraction was obtained by wet-

screening of the dispersed soil. (c) Material less than 0.4 mm. but which retained its cellular structure. This fraction was determined by flotation in a tall glass tube to the walls of which the particles adhered as the liquid was lowered slowly. Each fraction of the material was dried at 105°C. and weighed. Data are presented to show the reliability of the method.

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# PHOSPHATE FIXATION—AN EXCHANGE OF PHOSPHATE AND HYDROXYL IONS

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The removal of phosphates from solution when a soluble phosphate is brought into contact with certain soils has been termed "phosphate fixation." The exact nature of this removal has been the subject of much consideration and study by soil specialists. To the practical farmer, a means of preventing excessive phosphate fixation in soils is important. To any scientist who is interested in the physicochemical phenomena of soils as well as the complex soil-plant systems whereby plants absorb nutrients, a knowledge of the mechanism of phosphate fixation in soils is likewise of primary interest.

A review of the literature leaves one somewhat confused. Whether phosphate fixation is due to chemical precipitation, to adsorption, or to both is not clear. It is recognized that phosphates are precipitated as calcium phosphates in alkaline soils, but these salts are soluble enough to supply phosphorus for plant growth unless fluorine and carbonates are present in sufficient quantities to form very insoluble fluoroapatite and complex calcium phosphocarbonates. Such fixation, however, has not been found to occur in acid podzolic soils.

Until recently, chemical precipitation was considered the primary cause of phosphate fixation in soils. The precipitation has been attributed largely to calcium and magnesium in calcareous soils and to iron, aluminum, and manganese in acid soils. In the latter it was thought that fixation of phosphate was due to a simple precipitation of  $\text{FePO}_4$  and  $\text{AlPO}_4$ . Truog (16) and McGeorge and Breazeale (6), however, have shown that the normal phosphates of iron and aluminum are readily available to plants. Their findings seem to eliminate the idea of simple precipitation as an explanation of phosphate fixation, because even relatively acid soils are low in soluble iron. An explanation of phosphate fixation on the basis of adsorption has been proposed. Since hydrated oxides of iron and aluminum found in soils have colloidal properties, adsorption of phosphate is probable. Instead of using the confusing term "adsorption" to designate this colloidal mechanism of phosphate retention, Mattson (7), Pugh (10, 11), and Ravikovich (12, 13) have used "anion exchange." By this term they mean that phosphate is substituted on the colloidal complex in place of some other anion, which is in solution in smaller quantities or which does not possess enough energy to hold its position on the colloidal complex in competition with the very active phosphate ions.

Stout (15), working with aluminosilicate minerals, kaolinitic in type, showed that there is a reversible ionic exchange between phosphate and hydroxyl ions.

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He was able to show a definite change in the crystal structure of kaolin due to phosphate fixation and, furthermore, to measure the amount of water formed when phosphate was fixed from a  $\text{H}_3\text{PO}_4$  solution. This indicated that hydroxyl ions which were definite components of the crystal structure were replaced by phosphate ions.

Murphy (9) found that kaolinite fixes large amounts of phosphate but only when the mineral is very finely ground. It is quite evident that this intense grinding exposes a considerable number of hydroxyl ions which become active in fixing phosphate by an anion exchange reaction. A more complete review of literature on this subject is given by one of us (8).

The purpose of this study was to determine whether or not phosphate fixation is an anion exchange reaction between phosphate and hydroxyl ions of the soil colloidal complex. Though particular attention was given to hydroxyl ions, some work was also done with silicate and fluoride anions.

### pH CHANGES

If phosphate fixation is an exchange of hydroxyl and phosphate anions, there should be a pH change, especially in certain simple mixtures of the two. When phosphate in the form of the salt of a strong base like potassium is added to a high fixing medium such as ferric hydroxide, the liberation of hydroxyl ions should result in the formation of KOH in sufficient quantities to alter the pH of the mixture.

Resulting pH changes were measured on three materials— $\text{Fe}(\text{OH})_3$ ; finely ground kaolin<sup>2</sup> (ball-milled 8 days); and the B horizon of Hermon fine sand, which is known to be a very high phosphate fixing soil.

A material- or soil-water ratio of 1:5 was used in all the suspensions, and  $\text{KH}_2\text{PO}_4$  was the soluble phosphate. Before mixing of the suspension and the phosphate solution, the pH of one was adjusted to that of the other, so that the pH values of both were very nearly the same. After 24 hours the pH of the mixture was determined and recorded as "pH after fixation." A Beckman glass electrode pH meter was used in making all pH determinations.

The effect of phosphate fixation by ferric hydroxide on the pH of the mixture when various amounts of  $\text{K}_2\text{HPO}_4$  were added is shown in table 1. Phosphate fixation resulted in an increase in the pH of the  $\text{Fe}(\text{OH})_3$  suspensions, both when the pH of the  $\text{Fe}(\text{OH})_3$  was adjusted to that of the  $\text{KH}_2\text{PO}_4$  solution and when the pH of the  $\text{KH}_2\text{PO}_4$  solution was adjusted to that of the  $\text{Fe}(\text{OH})_3$  before mixing. Though pH changes cannot be used as a quantitative measure of phosphate fixation, the fact is that in the lower range they became greater as phosphate usage increased.

Similarly the effect of phosphate fixation by kaolin as measured by change in pH is shown in table 2. Phosphate fixation increased the pH of the kaolin-phosphate mixture. Smaller increases in pH were observed with kaolin than with  $\text{Fe}(\text{OH})_3$ , primarily because the latter fixes much more phosphate. The ability of kaolin to take up some potash would tend to decrease the basicity of

<sup>2</sup> Kaolin obtained from Ward's Natural Science Establishment.

the mixture. In spite of the possible absorption of potash, the change in pH is sufficient to indicate a similarity in the nature of phosphate fixation by  $\text{Fe}(\text{OH})_3$  and by finely ground kaolin. In either case, fixation is probably due to an exchange of exposed hydroxyl ions by the phosphate ions.

TABLE 1

*Changes in pH resulting from phosphate fixation when a solution of  $\text{KH}_2\text{PO}_4$  and a suspension of  $\text{Fe}(\text{OH})_3$  of similar pH are mixed*

PHOSPHATE ADDED ( $\text{PO}_4$ )	pH BEFORE FIXATION		pH AFTER FIXATION	CHANGE IN pH OF THE MIXTURE
	$\text{Fe}(\text{OH})_3$ Suspension	$\text{KH}_2\text{PO}_4$ Solution		
mgm.				
1.257	4.85	4.95	5.05	+0.20
2.758	4.65	4.95	5.55	+0.90
4.331	4.85	4.95	6.10	+1.25
5.515	4.65	4.95	6.20	+1.55
50.900	8.70	8.70	10.15	+1.45

TABLE 2

*Changes in pH resulting from phosphate fixation when a solution of  $\text{KH}_2\text{PO}_4$  and a kaolin suspension of similar pH are mixed*

PHOSPHATE ADDED ( $\text{PO}_4$ )	pH BEFORE FIXATION		pH AFTER FIXATION	CHANGE IN pH OF THE MIXTURE
	Kaolin suspension	$\text{KH}_2\text{PO}_4$ solution		
mgm.				
1.5	5.70	5.55	5.85	+0.15
3.0	5.70	5.55	6.00	+0.30
4.5	5.55	5.55	6.00	+0.45
6.0	5.55	5.55	6.10	+0.55

TABLE 3

*Changes in pH resulting from phosphate fixation when a solution of  $\text{KH}_2\text{PO}_4$  and a soil\* suspension of similar pH are mixed*

PHOSPHATE ADDED ( $\text{PO}_4$ )	pH BEFORE FIXATION		pH AFTER FIXATION	CHANGE IN pH OF MIXTURE
	Soil suspension	$\text{KH}_2\text{PO}_4$ Solution		
mgm.				
1.532	4.05	4.00	4.30	+0.25
3.064	4.05	4.00	4.30	+0.25
5.515	4.15	4.10	4.55	+0.40
6.128	4.05	4.00	4.30	+0.25
127.415	4.15	4.10	4.35	+0.20

\* Hermon fine sand.

Similar but smaller pH changes were obtained when the soluble phosphate was added to a suspension of high phosphate fixing soil, Hermon fine sand, of similar pH (table 3). Here again the pH value of the soil-phosphate mixture was greater than those of the individual components, despite the fact that this

soil is known to absorb large amounts of potash. In soils which absorb more potash than phosphate, the pH of the mixture would be lowered rather than raised.

The podzol soil used here contains relatively large amounts of hydrated iron oxides as evidenced by its brownish-red color. It seems likely that at least part of its phosphate-fixing capacity is due to its ability to absorb phosphate in exchange for the hydroxyl ions, as evidenced by the pH changes indicated in table 3.

TABLE 4

*Effect of dehydration by heating on the fixation of phosphate by soils and by anhydrous and hydrated oxides of iron and aluminum*

SAMPLE	TREATMENT	PROSPHORUS IN SAMPLE (P)	PROSPHORUS ADDED (P)	PROSPHORUS EXTRACTED (P)	PROSPHORUS FIXED (P)
		<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>per cent</i>
Hermon fine sand	No heat	6	400	24	95.5
	305°C., 5 days*	14	400	40	93.5
	White heat, 3 hours	52	400	320	33.0
Vergennes clay loam	No heat	77	400	320	39.2
	350°C., 5 days*	184	400	400	46.0
	White heat, 3 hours	260	400	560	25.0
Ferric hydroxide	No heat	0	400	0	100.0
	White heat, 3 hours	0	400	400	0.0
Anhydrous ferric oxide	No heat	0	400	400	0
	White heat, 3 hours	0	400	400	0
Aluminum hydroxide	No heat	12	400	300	28.0
	White heat, 3 hours	0	400	6	98.5
Anhydrous alu- minum oxide	No heat	0	400	6	98.5
	White heat, 3 hours	0	400	6	98.5

\* 350°C. was obtained by use of a molten lead bath.

#### DEHYDRATION

If exchangeable hydroxyl ions cause phosphate fixation, it should be possible to remove these ions by the use of high temperatures, as for example in dehydration. In order to determine the importance of the state of hydration as a factor in phosphate fixation, two soils and two iron and two aluminum oxides were heated at different temperatures. The phosphate-fixing capacities of the materials before and after heating, as determined by the method of Heck (5), are shown in table 4.

When ferric hydroxide was heated at white heat it lost its hydroxyls as water, and its phosphate-fixing capacity decreased from 100 per cent to 0. After heating, it resembled anhydrous ferric oxide, which fixed no phosphate at any time.

Since Hermon fine sand contained considerable amounts of hydrated ferric oxide, heating at white heat greatly decreased its capacity to fix phosphate. Aluminum hydroxide, on the other hand, fixes very little phosphate, but with the gradual loss of water on heating, fixation increases, as was found by Ford (3) in the case of bauxite. Anhydrous aluminum oxide fixes large amounts of phosphate in an insoluble form. No explanation for the variance between ferric hydroxide and aluminum hydroxide is offered. The decrease in phosphate fixation by Vergennes clay loam due to white heat was very small, presumably because the increase in fixation by dehydration of aluminum oxides almost offsets the decrease due to dehydration of ferric oxides. Most soils contain only the hydrated forms of iron and aluminum compounds, as the anhydrous oxides do not form under natural conditions in agricultural soils. If soil contains a large amount of hydrated iron oxide, heating at high temperatures will decrease its fixation; if soil contains large amounts of hydrated aluminum oxides, heating may actually increase its fixing capacity for phosphates. The behavior of the

TABLE 5

*Effect of removal of free iron and aluminum oxides on the ability of soils to fix phosphorus*

SAMPLE	TREATMENT	PHOSPHORUS IN ORIGINAL (P)	PHOSPHORUS ADDED (P)	PHOSPHORUS EXTRACTED (P)	PHOSPHORUS FIXED (P)
		<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>per cent</i>
Hermon fine sand	None	6.0	400	24	95.50
	R <sub>2</sub> O <sub>3</sub> * removed	0.0	400	350	19.25
Vergennes clay loam	None	77.0	400	320	39.25
	R <sub>2</sub> O <sub>3</sub> * removed	34.0	400	325	28.50

\* The removal of R<sub>2</sub>O<sub>3</sub> resulted also in the removal of silica, calcium, magnesium, and potassium from the soil.

soils on heating is further evidence that the phosphate is at least partly fixed by replacing hydroxyl ions.

#### REMOVAL OF SESQUIOXIDES

If phosphate fixation is due primarily to the formation of difficultly available compounds with the iron and aluminum oxides in the soil, removal of these oxides should reduce the degree of fixation. The phosphate-fixing capacity was determined, therefore, on two soils before and after the free iron and aluminum oxides were removed by the sodium sulfide-oxalic acid treatment of Drosdoff and Truog (2). The results are shown in table 5. When the free iron and aluminum oxides were removed, the phosphate-fixing capacity of Hermon fine sand was greatly reduced. As has been mentioned, this high phosphate fixing soil is known to contain considerable hydrated iron. The fixing capacity of Vergennes clay loam, however, was only slightly affected by the treatment. This indicates that very little hydrated iron oxide was causing fixation in the latter soil.



## ANION SUBSTITUTION

A number of writers, including Stout (15) and Ravikovitch (13), have suggested that phosphate fixation is a reversible reaction and that there is a definite anion exchange. The hydroxyl ion has received considerable attention and seems to be the most successful in replacing, or at least bringing into solution, the greatest amount of fixed phosphorus. The effect of increasing pH of extracting solution (increase in hydroxyl ions) on the liberation of previously

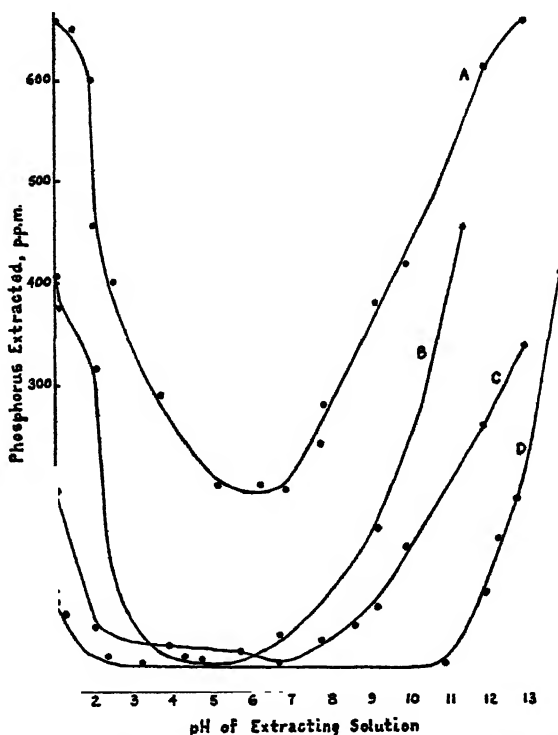


FIG. 1. EFFECT OF pH OF EXTRACTING SOLUTION ON LIBERATION OF PREVIOUSLY FIXED PHOSPHATE IN TWO SOILS AND TWO IRON COMPOUNDS

A, Vergennes clay loam; B, Hermon fine sand; C, Limonite; D, Ferric hydroxide. To each material 400 p.p.m. of phosphorus had been added and allowed to become fixed before extraction.

fixed phosphates in different materials was studied, Vergennes clay loam, Hermon fine sand, limonite,<sup>3</sup> and ferric hydroxide being treated with 400 p.p.m. of soluble phosphorus. After the phosphorus was allowed to become fixed by the Heck method (5), the materials were extracted by the Truog method (16) substituting buffered solutions of differing pH values. To obtain the desired pH for the extracting solution, various amounts of  $H_2SO_4$ -NaOH were used. These results are shown in figure 1.

<sup>3</sup> The limonite used was a bog ore variety obtained from Bolton, Quebec.

With the most alkaline extracting solutions, more phosphorus was removed than was added in the two soils used. It seems evident that all the fixed phosphate as well as much of the organic phosphorus in these soils was extracted. Even with limonite and ferric hydroxide, nearly all the fixed phosphate was extracted. In all cases the alkaline range was more effective in liberating phosphate than was the equivalent acid range. Of course, it is difficult to differentiate between the dissolving action and the replacing action of the hydroxyl ions at high pH values. Since there is a marked similarity between limonite and Hermon fine sand in the amount of phosphorus liberated at the various pH levels, the indication is strong that the mechanism of phosphate fixation in the two are very similar.

In addition to the hydroxyl ion, a number of other anions seem to be able to replace some fixed phosphate. The silicate ion seems to be very effective, as Schollenberger (14), Gile and Smith (4), Weiser (17), and many others have observed its beneficial effect on plant growth and phosphate recovery. More re-

TABLE 6

*Changes in pH due to anion fixation when a solution of  $\text{NH}_4\text{F}$  or  $\text{Na}_2\text{SiO}_3$  and a suspension of  $\text{Fe}(\text{OH})_3$  are mixed*

ANION	AMOUNT ADDED	pH BEFORE FIXATION		pH AFTER FIXATION	CHANGE IN pH OF MIXTURE
		$\text{Fe}(\text{OH})_3$ suspension	Anion solution		
Fluoride	<i>mgm</i>				
	0.5	5.90	5.90	6.60	+0.70
	1.0	5.90	5.90	6.65	+0.75
	2.0	5.90	5.90	6.65	+0.75
Silicate	1.0	6.30	6.30	6.65	+0.35

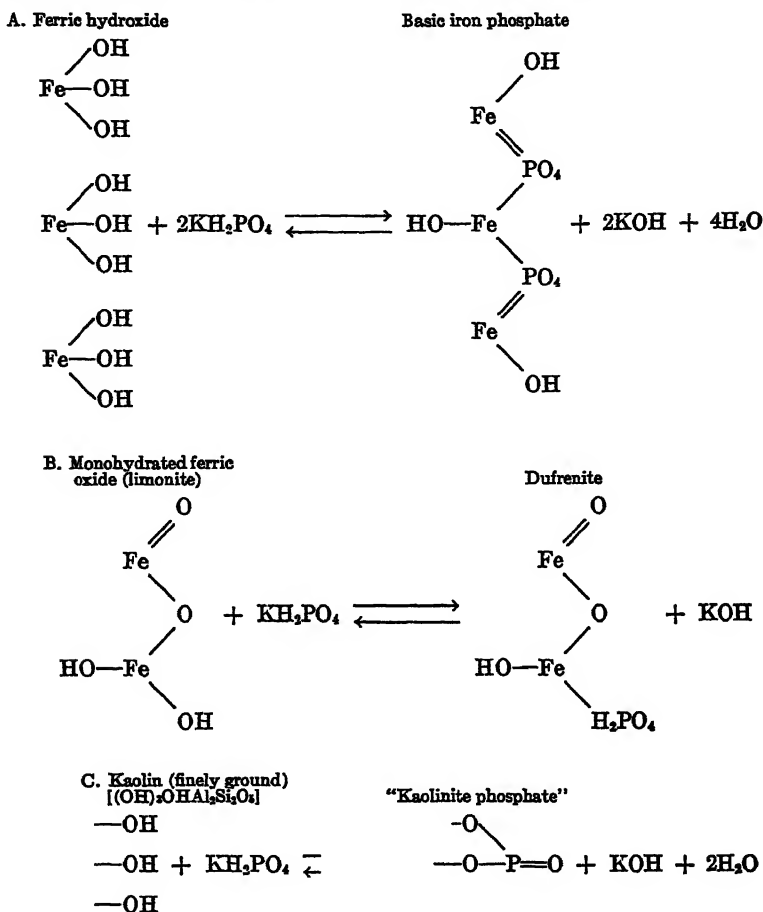
cently the fluoride ion was used by Dickman and Bray (1) to replace that portion of phosphate in soils which they call "adsorbed phosphate." If the silicate and fluoride ions are effective in replacing adsorbed phosphate, it seems probable that they should also replace the hydroxyl ion from  $\text{Fe}(\text{OH})_3$  and thus effect a change in pH. This was studied by the use of  $\text{NH}_4\text{F}$  and  $\text{Na}_2\text{SiO}_3$  in a manner similar to that with  $\text{KH}_2\text{PO}_4$  (see table 1). The results are presented in table 6. These results indicate that both silicate and fluoride ions are fixed with the liberation of hydroxyl ions, which increase the pH of the mixture.

#### MECHANISM OF PHOSPHATE FIXATION

The mechanism of phosphate fixation is apparently the same with hydrated sesquioxides as with finely ground kaolin. In both, it represents a physicochemical anion exchange equilibrium whereby phosphate ions replace exposed hydroxyl ions from the colloidal materials.

The increase in pH of a colloidal system caused by phosphate fixation is taken

as evidence that such an exchange of anions takes place. The possible exchange reactions may be represented by the following equations:



These seem to be equilibrium reactions, as is evidenced by the fact that fixed phosphate can be liberated when the hydroxyl ions exceed the concentration of phosphate ions in solution. To obtain complete liberation of phosphate ions, however, a very high concentration of hydroxyl ions must be present.

The fixation of silicate and fluoride ions by soils seems to be by the same mechanism as that of phosphate fixation. The beneficial effect of these two anions on plant growth is due to a lowering of the phosphate-fixing capacity of the soil, thus causing increased availability of applied phosphates. When the concentration of silicate or fluoride ions is high, these anions may replace phosphate ions, as was shown by Weiser (17) and by Dickman and Bray (1).

#### DISCUSSION AND SUMMARY

Most soils contain a considerable amount of iron oxide distributed as a film over individual soil particles. This is especially true of the lateritic and podzolic

soils (B horizon). Though this hydrated iron oxide is not in solution, its colloidal nature and its surface position on soil particles make it very active in fixing any soluble phosphate that comes in contact with it. Data presented in this paper indicate that phosphate fixation is a physicochemical exchange of phosphate ions for these exposed hydroxyl ions. Though this seems to be an equilibrium reaction, in soils it is greatly shifted toward phosphate fixation, because of the very low hydroxyl-ion concentration in the soil solution and the high hydroxyl concentration of the hydrated ferric oxides on the surface of the soil particles. Kaolin fixes phosphate only when it is finely ground to expose active hydroxyl ions. Ferric hydroxide, finely ground kaolin, and a podzol B horizon were found to fix large amounts of phosphate in an unavailable form. When a suspension of any of these materials was mixed with soluble phosphate of similar pH, the resultant mixture increased in pH. This is taken to indicate that phosphate ions replaced the hydroxyl ions.

Dehydration and removal of hydroxyl ions by high temperatures greatly reduced the phosphate-fixing capacity of soils and of hydrated iron oxide. The reverse is true for hydrated aluminum oxide.

Removal of active iron and aluminum ( $R_2O_3$ ) also greatly reduced the capacity of soils to fix phosphate.

Both silicate and fluoride ions are capable of replacing hydroxyl ions, as evidenced by pH changes. The beneficial effect of silica on plant growth may be due to its ability to remove fixed phosphate or to replace the hydroxyl ions and thus decrease phosphate fixation.

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# DISTRIBUTION OF TOTAL AND ALKALI-SOLUBLE ORGANIC MATTER BETWEEN THE WHOLE SOIL AND SOIL AGGREGATES OF DUNMORE SILT LOAM: I. INFLUENCE OF FERTILITY TREATMENTS 6 AND 18 MONTHS AFTER LIMING<sup>1</sup>

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Crop residues and manure are incorporated in cultivated soil to maintain the supply of organic matter, which in turn preserves soil tilth. It is important to determine the conditions under which soil structure is most benefited from such maintenance. From the standpoint of soil conservation we are interested in cementing the large soil aggregates with organic matter in order to reduce losses of inorganic and organic fractions by erosion. Because knowledge of the chemical composition of organic matter is limited, however, and the specific constituents involved in aggregation are not known, studies of the relationship of organic matter to soil aggregation must be general.

Many investigators (3-10, 12) have reported that organic matter serves as a cement in binding the soil particles into water-stable aggregates. It has also been reported (11, 15) that the addition of alkali "humate" extracts to mineral soils results in stable aggregate formation.

The purpose of the study reported here was to investigate the distribution of the total and alkali-soluble organic matter between the soil aggregates and the whole soil from which they were formed.

## EXPERIMENTAL METHODS

Soil samples were taken 6 and 18 months after ground limestone at the rate of 2 tons per acre had been applied to 96 fertility plots on Dunmore silt loam in the spring of 1940. A diagram of the layout of the plots with the agronomic treatments was previously presented (2). One-half of the plots had been treated yearly since 1914, and of these, 32 received various kinds and amounts of commercial fertilizers, whereas 16 received applications of manure; the other 48 subplots had been untreated during this period. After the soil had been sampled, two aggregate-size groups (1.0-2.0 and 0.10-0.25 mm. designated as large and small aggregates respectively) were separated by wet-screening (1).

Whole soil and soil aggregates were ground to pass a 100-mesh sieve, and the total organic matter was determined on these materials by wet oxidation with chromic acid (13). Alkali-soluble organic matter was determined as that por-

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tion of the organic matter soluble in hot 0.1 *N* NaOH.<sup>3</sup> Five grams of the ground material and 50 cc. of 0.1 *N* NaOH were placed in a 125-cc. Erlenmeyer flask and heated on the steam bath for 2 hours; a small funnel placed in the neck of the flask acted as a condenser. After extraction, the alkali-soluble fraction was removed by filtering with suction through one thickness of Whatman #41 filter paper and by washing the material successively with 50- and 25-cc. portions of boiling water, employing decantation. The soil material was then dried, re-ground, and the alkali-insoluble fraction of the organic matter determined by wet oxidation with chromic acid. Alkali-soluble organic matter was computed as the difference between the organic matter in the original ground material and that remaining after extraction with hot dilute alkali.

#### RESULTS AND DISCUSSION

On the basis of 1940 data it was reported (2) that the whole soil and soil aggregates from the treated subplots (manured and fertilized) contained more organic matter than the untreated ones and the manured subplots more than those that were fertilized. Similarly, total organic matter for 1941 and alkali-soluble organic matter for 1940 and 1941 showed highly significant differences between the treated subplots and untreated ones and between the manured subplots and those fertilized. Mean values for the treatments and differences between treatments 6 and 18 months after liming are presented in table 1. It should be observed that the magnitude of the differences for the treatments remained the same for the two seasons. It will also be seen that there were seasonal variations in the amount of total and alkali-soluble organic matter in the soil and aggregates. No attempt will be made to explain these variations, as the experimental arrangement and method of sampling did not warrant such an analysis of the data.

In the surface horizon of a virgin soil or of a long-established sod the individual soil separates of sand, silt, and clay are coated with organic matter. As these separates become incorporated into soil aggregates, the resulting structural particles contain organic matter on the inside of the aggregates as well as a coating on the outside of the agglomerates. After the soil is brought under cultivation, these aggregates are destroyed and the organic matter of the soil and of the aggregates is depleted. As a result of this depletion the aggregates that form under arable conditions contain much less organic matter. It should be observed from the data in table 1 that as a result of the incorporation of manure or crop residues in the treated subplots, the organic matter content of the soil and of the large and small aggregates was maintained. The manure treatments appeared to be more effective than the fertilizer treatments. A question then naturally is raised whether there is any direct relationship between the organic matter content of the aggregates and that of the whole soil from which the aggregates were derived.

To answer this question the experimental data were further studied by the

<sup>3</sup> This extracting medium was selected because of the report of other investigators (14) that an arbitrary fraction of the organic matter is thus made soluble.

analysis of covariance to determine (a) whether the highly significant treatment differences for the alkali-soluble organic matter in the whole soil and soil aggregates could be explained by the regression of alkali-soluble organic matter on total organic matter, (b) whether the treatment differences for the total or alkali-soluble organic matter in the large and small aggregates could be explained by the regression of these variables on the whole soil, and (c) whether the treatment differences for the total or alkali-soluble organic matter in the small ag-

TABLE 1

*Total and alkali-soluble organic matter in whole soil and soil aggregates of Dunmore silt loam 6 and 18 months after liming*

Results in percentage of dry matter

PLOTS	PERIOD AFTER LIMING					
	6 months			18 months		
	Soil	1.0 mm.	0.1 mm.	Soil	1.0 mm.	0.1 mm.
<i>Total organic matter</i>						
Treated*.....	2.73	2.67	2.75	2.72	2.55	2.60
Untreated†.....	2.19	2.17	2.14	2.21	2.06	1.99
Difference.....	0.54	0.50	0.61	0.51	0.49	0.61
Manured‡.....	3.35	3.25	3.34	3.29	3.07	3.12
Fertilized§.....	2.42	2.38	2.45	2.44	2.29	2.34
Difference.....	0.93	0.87	0.89	0.85	0.78	0.78
<i>Alkali-soluble organic matter</i>						
Treated*.....	1.55	1.56	1.47	1.47	1.46	1.44
Untreated†.....	1.25	1.24	1.16	1.21	1.21	1.13
Difference.....	0.30	0.32	0.31	0.26	0.25	0.31
Manured‡.....	1.97	1.91	1.77	1.80	1.74	1.74
Fertilized§.....	1.34	1.39	1.32	1.30	1.32	1.29
Difference.....	0.63	0.52	0.45	0.50	0.42	0.45
	56.9§	57.9§	53.7§	54.3§	58.3§	55.9§

\* Mean of 48 plots (32 fertilized and 16 manured).

† Mean of 48 plots.

‡ Mean of 16 plots.

§ Mean of 32 plots.

§ Percentage of total organic matter. Mean of 96 plots (48 treated and 48 untreated).

gregates could be explained by the regression of small aggregates on large aggregates. In table 2 are shown a summary of the regressions, indicating those that were significant.

#### *Relationship between total and alkali-soluble organic matter*

In general, the regression of alkali-soluble organic matter on total organic matter was significant (table 2). This relationship did not hold for the small



aggregates in 1940. This was related to the fact that after 6 months only 53.7 per cent (table 1) of the total organic matter in the 0.1-mm. aggregates was alkali-soluble. On the other hand, 18 months after liming when the alkali-soluble and total organic matter in the small aggregates were related, 55.9 per cent of the total was alkali-soluble.

*Effect of treatment on total organic matter in whole soil and soil aggregates*

It was mentioned that a highly significant effect of treatment was the maintenance of more organic matter in the soil from the treated subplots than in that from the untreated ones. It was natural to expect a similar treatment effect

TABLE 2

*Regressions for total and alkali-soluble organic matter in whole soil and soil aggregates 6 and 18 months after liming*

	TREATMENT COMPARISON			
	Treated vs. Untreated		Manured vs. Fertilized	
	6 months	18 months	6 months	18 months
<i>Total vs. alkali-soluble organic matter</i>				
Whole soil.....	+	+	+	+
Large aggregates.....	+	+	+	+
Small aggregates.....	-	+	-	+
<i>Total organic matter</i>				
Whole soil vs. large aggregates.....	+	-	+	-
Whole soil vs. small aggregates.....	-	-	+	+
Large vs. small aggregates.....	-	-	+	+
<i>Alkali-soluble organic matter</i>				
Whole soil vs. large aggregates.....	-	-	+	-
Whole soil vs. small aggregates.....	+	-	+	+
Large vs. small aggregates.....	+	-	+	-

+ Regression significant.

- Regression not significant.

on the large and small aggregates from the treated subplots. For this reason it was of interest to determine the conditions under which the treatment effect in maintaining the organic matter content of the soil aggregates was related to a similar treatment effect on the whole soil.

Six months after liming the regressions of the treatment comparisons (treated vs. untreated and manured vs. fertilized) for the large aggregates on those for the whole soil were significant (table 2). Although after 18 months this was not the case, further study will be necessary to establish whether the significant regressions during the 6-month period were caused by liming.

The regressions of the treatment difference (treated vs. untreated) for small aggregates on whole soil or large aggregates were not significant in either period.

In both the 6- and 18-month periods the treatment difference was greater for the small aggregates than for the whole soil or large aggregates. For both periods, however, the regressions of the treatment difference (manured vs. fertilized) for small aggregates on whole soil or large aggregates were significant. This was related to the fact that the treatment difference was not greater for the small aggregates than for the whole soil or large aggregates.

*Effect of treatment on alkali-soluble organic matter in whole soil and soil aggregates*

In both periods the regression of treatment difference (treated vs. untreated) for the large aggregates on that for the whole soil was not significant (table 2). This indicated that there was little relationship between the soil and large aggregates in content of alkali-soluble organic matter. An explanation of the lack of significant regression may be based on the composition of the organic matter with respect to the alkali-soluble fraction. Six months after liming, the soil contained 56.9 per cent alkali-soluble organic matter, which dropped to 54.3 per cent after 18 months (table 1). In the large aggregates, however, the percentage of total organic matter that was alkali-soluble remained almost constant for the two periods (57.9 after 6 months and 58.3 after 18 months). It appeared that a fraction of the organic matter that was alkali-soluble collected in the large aggregates. This accumulation was not wholly associated with the fraction in the whole soil.

Six months after liming there was good agreement for the treatment difference (treated vs. untreated) for the comparison of small aggregates vs. whole soil or vs. large aggregates. After 18 months this agreement had largely disappeared.

*Manure vs. fertilizer treatments*

It should be noted for both the 6- and 18-month periods (table 2) that many of the regressions of the whole soil vs. large or small aggregates were significant for the treatment comparison, manure vs. fertilizer. It was mentioned that the manure treatments were more effective than the fertilizer treatments in maintaining the total as well as the alkali-soluble organic matter content of the soil and aggregates (table 1). Nevertheless, both of these treatments were effective in maintaining the organic matter content of the soil, a fact that was correlated in nearly all cases with an increased amount of organic matter in the large and small aggregates.

SUMMARY

Total and alkali-soluble (hot 0.1 N NaOH) organic matter were determined on the whole soil and on large and small aggregates (1.0–2.0 mm. and 0.10–0.25 mm. respectively) separated from the soil of 96 long-time fertility plots on Dunmore silt loam 6 and 18 months after liming.

Whole soil and both aggregate-size groups from the treated subplots (manured or fertilized) contained more alkali-soluble organic matter than the untreated ones, and the manured more than the fertilized. This was explained by the presence of more total organic matter in the soil and soil aggregates from the

treated subplots than in the untreated ones, and more in the manured than in the fertilized subplots.

The total organic matter data showed that the regressions of the treatment difference (treated vs. untreated) for the small aggregates on whole soil or on large aggregates were not significant in either period.

The alkali-soluble organic matter showed that in both the 6- and 18-month periods the regression of treatment difference (treated vs. untreated) for the large aggregates on that for the whole soil was not significant. An explanation was based on the fact that the percentage of the total organic matter in the large aggregates that was alkali-soluble was fairly constant and independent of the composition of the whole soil. The percentages were 57.9 after 6 months and 58.3 after 18 months for the aggregates, whereas those for the whole soil fell from 56.9 to 54.3 for the corresponding periods. Six months after liming there was good agreement for the treatment difference (treated vs. untreated) for the comparisons small aggregates vs. whole soil or vs. large aggregates. After 18 months, these same comparisons showed little relationship.

Fertilizer treatments as well as manure treatments maintained the total and the alkali-soluble matter content of the whole soil. This was correlated in nearly all cases with an increased amount of organic matter in the large and small aggregates.

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# QUALITATIVE STUDIES OF SOIL MICROORGANISMS: V. NUTRITIONAL REQUIREMENTS OF THE PREDOMINANT BACTERIAL FLORA<sup>1</sup>

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Though microorganisms concerned with known biochemical processes in the soil have been widely studied, much less attention has been paid to groups of bacteria of which the functions are still largely unknown or but little understood, but which doubtless comprise a large proportion of the indigenous microflora of arable soils. Investigations of the latter groups have been hampered by lack of satisfactory methods for their isolation and of criteria for their classification, both morphological and physiological. Thus in contrast to those organisms concerned with known functions, they require for their isolation as nonselective a medium as possible, in order that "representative" types may develop with the least suppression by other special groups that might be favored by the incorporation in the medium of special energy sources. The procedure is essentially qualitative, though the value of such is greatly enhanced when at the same time quantitative aspects can be taken into account in establishing the relative incidence in any given soil of the various qualitative groups.

For classification of the indigenous soil bacteria on a physiological basis, it is becoming more apparent that the "classical" biochemical tests are inadequate for any rational grouping helpful to an understanding of the activity or significance of these organisms in soil. Furthermore, as Lochhead and Taylor (3, 7) have pointed out, the majority of soil bacteria display a relatively low degree of biochemical activity, as judged by standard laboratory tests, and are regarded as being comparatively unstable physiologically. Hence, other physiological criteria are felt to be more suited to their grouping.

It is self-evident that the equilibrium between various groups of organisms existing in any soil at any given time will depend in large measure upon the availability of nutrients required for the growth of those organisms. Though special antagonisms and the presence of toxic factors may distort this relationship, in the main the relative incidence of a group of microorganisms requiring, for example, a special growth factor will depend upon the presence of that factor in the soil. By classifying organisms according to certain nutritional needs, West and Lochhead (10) suggested a method for measuring the bacterial equilibrium in soil. This method has been applied to advantage by West and Hildebrand (1, 11) in studying the relationship of the soil microflora to strawberry root rot disease and its control. The procedure consisted in observing the growth response of soil bacteria, isolated by nonselective plating methods, in

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three media of varying complexity—basal, amino acid, and growth factor media. The present studies were planned to examine more extensively the nutritional requirements of soil bacteria, with consideration also of those for which the above media are inadequate.

#### EXPERIMENTAL

The organisms studied were isolated from soils of a 4-year rotation system of oats, clover, timothy, and mangels. One soil (N) had been impoverished by continuous cropping without fertilizer addition; the other (X) had been maintained at good fertility level by regular application of farmyard manure. Samples were taken from each soil in June and in October, 1941.

Cultures were obtained by plating on a nonselective soil extract agar medium according to methods previously described (4, 7). Colonies were systematically picked so that all on a plate or a sector were taken, and stab cultures were made into soil extract semisolid (containing 0.02 per cent  $K_2HPO_4$ , 0.01 per cent yeast extract, and 0.3 per cent agar) for further study.

#### *Media for nutritional grouping*

For a comparative study of the nutritional requirements of the isolates seven media, as follows, were used:

Basal medium (*Medium B*): glucose 1.0 gm.;  $K_2HPO_4$ , 1.0 gm.;  $KNO_3$ , 0.5 gm.;  $MgSO_4$ , 0.2 gm.;  $CaCl_2$ , 0.1 gm.;  $NaCl$ , 0.1 gm.;  $FeCl_2$ , 0.01 gm.; distilled water, 1 liter. Heat to  $100^\circ C$ ., filter, and adjust reaction to pH 6.8.

Amino acid medium (*Medium A*): basal medium plus 0.05 gm. per liter each of cysteine, alanine, proline, asparagine, glutamic acid, aspartic acid, arginine, leucine, glycine, and lysine.

Growth factor medium (*Medium G*): basal medium plus cysteine, 0.05 gm.; thiamin, 100  $\mu gm$ .; biotin, 0.1  $\mu gm$ ; pyridoxin, 200  $\mu gm$ .; pantothenic acid, 100  $\mu gm$ .; nicotinic acid, 100  $\mu gm$ .; riboflavin, 200  $\mu gm$ .; and inositol, 0.05 gm. per liter.

Amino acid + growth factor medium (*Medium AG*): basal medium plus amino acids as in medium A and growth factors as in medium G.

Yeast extract medium (*Medium Y*): basal medium + yeast extract (Difco), 1.0 gm. per liter.

Soil extract medium (*Medium S*): 750 ml. basal medium plus 250 ml. soil extract, prepared by autoclaving 1 kgm. soil with 1 liter water for 30 minutes, filtering after adding a little  $CaSO_4$ , and making filtrate up to 1 liter.

Yeast + soil extract medium (*Medium YS*): soil extract medium plus 1.0 gm. yeast extract per liter.

All media were tubed in 5-ml. amounts. Transfers of each organism were made by loop inoculation from soil extract semisolid. Cultures were incubated at  $26^\circ$ – $28^\circ C$ . for 5 days and the growth responses of each isolate in the seven media recorded by assigning a turbidity value of 4 to the tube showing heaviest growth and rating the others by comparison. To avoid assigning too great importance to small variations, a difference of not less than 2 points was considered significant. Readings of 1 and 2 were regarded as showing submaximal growth.

On the basis of their growth in the seven media, the organisms could be divided into the following groups:

I. *Bacteria with simple requirements.* These bacteria show good growth in medium B and are therefore capable of synthesizing their requirements for maximum growth from ingredients of the glucose-nitrate-salts medium. Growth is not significantly better in any of the other media.

II. *Bacteria requiring one or more amino acids.* These organisms grow well in medium A but show either no growth or submaximal growth in medium B. Those which grow equally well in medium A and G obviously require only cysteine since this is common to both. The majority of those showing maximum development in A, however, do not grow well in G, indicating a need for one or more of the other amino acids present in the medium.

III. *Bacteria which require growth factors.* These bacteria produce maximum growth in medium G but none or submaximal growth in B or A. Previous work (9) has shown that response to growth factors occurs best in the presence of cysteine, and that the more important growth factors are thiamin and biotin.

IV. *Bacteria requiring amino acids plus growth factors.* The bacteria in this group show maximum development in medium AG, but show no growth or only submaximal growth in B, A, or G. Evidently, in addition to one or more growth factors, these organisms require one or more amino acids of medium A apart from cysteine.

V. *Bacteria requiring unidentified substances in yeast extract.* These organisms show maximum growth in medium Y, but fail to grow, or develop only slightly, in B, A, G, or AG. In the soil extract medium (S) growth in the great majority of cases is absent or meager, though a few members of the group show growth equal to that in Y.

VI. *Bacteria requiring unidentified substances in soil extract.* Organisms of this group are capable of maximum development in medium S, but show none or submaximal growth in B, A, G, AG, or Y.

VII. *Bacteria requiring unidentified substances in both yeast extract and soil extract.* These bacteria are capable of maximum development only in medium YS. In all of the media B, A, G, AG, Y, and S, growth is either absent or submaximal.

It is obvious that further classification into subgroups could be made on the basis of growth response in the media selected. Thus distinction could be made between organisms showing no growth and those capable of submaximal growth in the basal medium or in other media. For the main purpose of this report classification is based on the seven main groups.

#### *Incidence of different nutritional groups in soil*

The relative incidence of the various nutritional groups of bacteria in the soils studied is shown in table 1. In the fertile soil, organisms capable of developing in the basal medium, or indeed in the "synthetic" media of known composition (groups I to IV), were less abundant than in the poor soil (39.4 per cent as compared with 52.8 per cent). On the other hand forms for which the more complex ingredients of yeast and soil extract are necessary (groups V to VII) were relatively more numerous. Despite such differences, doubtless related to the higher content of organic matter in the better soil, the incidence of the different groups



does not appear to reflect markedly the pronounced difference in crop-producing capacity. The classification of bacteria on the basis of nutritional requirements, however, indicates certain differences between soils not brought out by classification based on morphology (7).

Table 1 also gives the bacterial groups as determined at different seasons. In October, organisms requiring amino acids and growth factors for maximum growth were less abundant than in June, a result which appears explicable in view of the effect of an actively growing crop. In other respects little differences between the two sampling dates were noted.

TABLE 1  
*Nutritional groups of soil bacteria in relation to fertility and season*

	SOIL N (INFERTILE)		SOIL X (FERTILE)		JUNE SAMPLING		OCTOBER SAMPLING	
Number of cultures on soil extract—yeast semi-solid.....	171		165		175		161	
	no.	per cent	no.	per cent	no.	per cent	no.	per cent
<i>Nutritional group</i>								
I. Good growth in basal medium.....	25	14.6	13	7.9	18	10.3	20	12.4
II. Require amino acids.....	14	8.4	20	12.1	18	10.3	16	9.9
III. Require growth factors.....	22	12.8	20	12.1	18	10.3	24	14.9
IV. Require amino acids and growth factors.....	29	17.0	12	7.3	29	16.6	12	7.5
V. Require yeast extract.....	16	9.4	37	22.4	24	13.7	29	18.1
VI. Require soil extract.....	12	7.0	5	3.0	11	6.3	6	3.7
VII. Require yeast and soil extract.....	50	29.2	53	32.1	51	29.1	52	32.3
No growth in test media.....	3	1.8	5	3.0	6	3.4	2	1.3

*Relation of nutritional groups to morphological types*

To note any relationship between the nutritional requirements of the organisms and their morphological grouping, all isolates were subcultured on a variety of media, and microscopic observations were made to permit of their classification into broad groups. For this purpose the general procedure of previous work (4) was followed. Special attention was given to the detection of pleomorphic forms related to the group of corynebacteria and which in many soils comprise a numerically important group.

As shown in table 2, the various nutritional groups of bacteria are not restricted to any definite morphological type of organism, but include for the most part representatives of various forms. Some of the less abundant morphological types, however, are restricted to certain groups, and certain trends in the distribution of the more abundant types are noted. Organisms with simpler requirements (groups I and II) consist to a rather larger extent of sporeforming rods and Gram-negative nonsporing rods. In the case of organisms requiring the more complex ingredients of soil extract (groups VI and VII), pleomorphic

forms comprise a greater percentage of the total. There is, however, no clear-cut correlation of morphology with nutritional needs.

*Relation to certain biochemical properties*

Table 2 also shows the relationship of the different nutritional groups to certain biochemical properties. To provide a medium suited to the growth of all organisms, a base of soil extract with 0.02 per cent  $K_2HPO_4$  and 0.01 per cent yeast extract was used. The test media contained respectively 0.1 per cent  $KNO_3$ , 1 per cent dextrose, and 10 per cent gelatin, the first two being semisolid (0.3 per cent agar).

TABLE 2

*Nutritional requirements of soil bacteria in relation to morphological type and some biochemical properties*

	NUTRITIONAL GROUP						
	I	II	III	IV	V	VI	VII
Total number of cultures.....	38	34	42	41	53	17	103
	per cent	per cent	per cent	per cent	per cent	per cent	per cent
<i>Morphological group</i>							
Cocci, Gram-positive.....	5.3	3.0	4.8	9.8	15.1	11.8	11.6
Cocci, Gram-negative.....	5.3	0.0	14.3	4.9	3.8	0.0	0.0
Rods, sporeforming.....	5.3	17.6	0.0	7.3	3.8	0.0	1.0
Rods, nonsporing, Gram-positive.....	10.5	11.8	19.0	29.3	13.2	11.8	8.7
Rods, nonsporing, Gram-negative.....	50.0	52.9	40.5	17.1	41.5	23.5	29.1
Pleomorphic, Gram-positive.....	23.7	11.8	21.4	31.7	17.0	41.2	46.6
Pleomorphic, Gram-negative.....	0.0	3.0	0.0	0.0	5.9	11.8	2.0
<i>Physiological group</i>							
Nitrate reduction.....	42.2	53.1	52.5	61.1	56.3	64.7	64.0
Gelatin liquefaction.....	67.6	80.7	72.5	66.0	52.2	41.2	57.8
Dextrose 1 per cent—acid.....	48.6	31.3	52.5	61.1	36.8	53.3	33.6
Dextrose 1 per cent—alkaline.....	46.0	31.3	7.5	5.6	14.3	0.0	44.5
Inhibited by 1 per cent dextrose.....	0.0	6.2	2.5	0.0	8.2	6.0	16.4

Ability to reduce nitrates, liquefy gelatin, or produce acid in dextrose does not appear to be associated with any group or groups. Considerable variation was noted in ability to produce an alkaline reaction in the dextrose medium. The effect of dextrose in suppressing growth of many soil bacteria, pointed out previously (7), was again noted. It is seen that the organisms inhibited by the presence of the sugar are mainly those with the most complex nutritional requirements, especially group VII.

ORGANISMS REQUIRING SOIL EXTRACT

The bacteria of groups VI and VII comprised those for which soil extract, with or without yeast extract, was required for maximum growth. Of the 120 cultures in these groups, 57 showed submaximal development in yeast extract

(medium Y). The remaining 63 cultures, comprising 19 per cent of the total isolates from soil, were unable to develop in medium Y (or in media B, A, G, AG or in one containing peptone with the addition of the growth factors) and were given special consideration. All grew well in medium YS, and of these, 8 showed equally good growth in soil extract without yeast (medium S), 42 gave submaximal growth, and 13 no growth.

The morphological distribution of the organisms of this group, indicated below, showed a higher proportion of pleomorphic bacteria and of Gram-positive cocci than any of the other nutritional groups:

	<i>per cent</i>
Cocci, Gram-positive.....	15.9
Cocci, Gram-negative.....	1.6
Rods, sporeforming.....	0.0
Rods, Gram-positive.....	3.2
Rods, Gram-negative.....	20.7
Pleomorphic, Gram-positive.....	57.3
Pleomorphic, Gram-negative .....	1.6

#### *Effect of treatment on soil extract*

Since all organisms grew well in soil extract with yeast extract (medium YS) and showed no growth with yeast extract alone (medium Y), comparisons were made with all organisms in these media and in various media containing yeast extract to which were added respectively preparations of soil extract subjected to different treatments. Such addenda included soil extract ash; acetone, alcohol, and ether extracts; the filtrate after treatment with Norit; the ammoniacal alcohol eluate of the Norit adsorbate; and a combination of charcoal filtrate and eluate. In all cases the addenda were made to correspond with the volume of soil extract present in the control medium YS.

The effects of the various treatments are summarized in table 3. Soil extract ash was able to provide substances required for maximum growth for only 1 organism, and to permit of submaximal growth, in most cases very slight, of 8 cultures. Of the various solvents used for extraction, acetone was the most effective. The acetone extract permitted growth of all but 11 organisms, 26 showing maximum development. Treatment of soil extract with alcohol was much less satisfactory. The ether extraction removed from soil extract substances suited to the growth of but 1 of the 63 cultures. Treatment with charcoal removed entirely the growth-promoting effect of soil extract for 49 of the cultures and partially for 11 organisms. Only 3 of the 63 cultures were capable of maximum growth with the charcoal filtrate.

Elution of the charcoal with alcohol yielded an eluate which permitted maximum or submaximal growth of 44 of the organisms. The results indicate that at least partial recovery of the adsorbed substances necessary for growth of the majority of the bacteria of this group could be made. A further test, in which the charcoal filtrate and eluate were both present, gave a still higher proportion

of the organisms showing growth. The results suggest either a multiple nature of the factors required for some organisms, or more probably, incomplete adsorption and elution respectively under the experimental conditions.

TABLE 3  
*Effect of various treatments on growth-promoting properties of soil extract*

ADDENDA TO YEAST EXTRACT (MEDIUM Y)	NUMBER OF ORGANISMS		
	No growth	Submaximal growth	Maximum growth
<i>Controls</i>			
Nil.....	63	0	0
Soil extract, untreated.....	0	0	63
<i>Soil extract fractions</i>			
Ash.....	54	8	1
Acetone extract.....	11	26	26
Alcohol extract.....	29	27	7
Ether extract.....	62	0	1
Charcoal filtrate.....	49	11	3
Charcoal eluate.....	19	36	8
Charcoal filtrate + eluate.....	9	38	16

*Extracts from soils of different fertility*

To note the effectiveness of extracts prepared from soils of different productivity, comparisons were made between the poor soil (N) and the fertile soil (X), the average relative crop-producing powers of which over a 5-year period were as follows:

	<i>Timothy</i>	<i>Mangels</i>	<i>Oats</i>	<i>Clover</i>
Soil N.....	64	9.5	72	42
Soil X.....	100	100	100	100

Tests were made with 15 organisms in media prepared with extracts of the two soils incorporated with medium Y. The results, given in table 4, show the pronounced difference in growth-promoting ability of the extracts from the two soils for most of the organisms tested. The good growth of certain cultures with the extract of the poor soil indicates the varied nature of the requirements of different organisms and that more than one growth-promoting substance may be present in soil extract.

*Growth-promoting effect of group I organisms*

Table 4 also includes results of a test to note whether the nutritive effect of soil extract could be replaced by a filtrate from cultures of bacteria of group I, capable of synthesizing their growth requirements from the ingredients of the basal medium. Five cultures of group I organisms selected at random were grown in medium B. When maximum growth was reached the cultures were combined

and passed through a Seitz filter. To 3 parts of medium Y, 1 part of filtrate was added. Five of the test organisms grew well and two others responded slightly to the addition of the filtrate, indicating that for some of the more fastidious soil bacteria the growth-promoting effect of soil extract could be supplied by metabolic products of other organisms having simpler requirements. This is of interest in view of the ability of certain soil microorganisms to produce auxins (5).

The filtrates used were ineffective for other test organisms, indicating distinctly different growth requirements and further suggesting the presence of more than one growth-promoting factor in soil extract. Since the number of

TABLE 4  
*Growth-promoting effect of extracts from soils of different fertility and of filtrates of group I organisms*

CULTURE NUMBER	RELATIVE GROWTH* IN MEDIUM Y PLUS ADDENDA			
	NH	Extract from poor soil (N)	Extract from fertile soil (X)	Filtrate from culture of bacteria of group I
1N13	0	2	4	0
1N18	0	0	4	4
1N51	0	4	4	3
1N69	0	0	4	0
1X17	0	0	4	0
1X21	0	0	4	0
1X55	0	0	4	0
1X67	0	4	4	0
2N2	0	0	4	0
2N7	0	2	4	1
2N11	0	0	4	3
2N18	0	0	4	0
2N20	0	0	4	1
2N40	0	0	4	4
2N58	0	0	3	4

\* A turbidity value of 4 indicates heavy growth; lower values indicate correspondingly less growth.

group I organisms used was small, it is by no means improbable that other members of this group would be able to furnish substances suited to other test organisms unable to grow with the filtrates provided. The results emphasize the interdependence of many members of the soil microflora.

#### DISCUSSION

The classification of soil bacteria on the basis of nutritional needs reveals the presence of groups, varying in requirements from simple to very complex, the relative incidence of which may be fairly constant in soils of given type. Any broad system of nutritional grouping, however, may give a false impression of uniformity in type of the members of a given group. Previous work on morphological and general biochemical classification (7) brought out the variability

inherent in apparently closely related types. The present nutritional studies emphasize the divergencies possible between members of the same group. The nutritional basis of grouping, however, serves as a better aid to any understanding of the function of the organisms in soil.

TABLE 5

*Nutritional requirements as indicated by growth\* in various media, of organisms of group IV (amino acids and growth factors)*

CULTURE NUMBER	CONTROL (MEDIUM AG)	AMINO ACIDS PLUS SINGLE GROWTH FACTORS							GROWTH FACTORS PLUS SINGLE AMINO ACIDS								
		Thiamin	Biotin	Pyridoxin	Pantothenic acid	Nicotinic acid	Riboflavin	Inositol	Alanine	Proline	Asparagine	Glutamic acid	Aspartic acid	Arginine	Leucine	Glycine	Lysine
1N1	4	2	2	0	0	2	0	0	0	3	0	0	0	3	1	0	0
7	4	0	1	1	0	0	2	0	0	0	0	0	0	1	1	0	0
8	4	3	4	1	2	1	2	2	2	2	4	3	4	4	2	3	2
9	4	4	4	4	1	1	2	1	4	1	1	2	1	1	1	1	1
14	4	1	2	0	0	0	0	0	0	0	1	0	0	0	4	1	1
15	4	1	1	0	0	0	1	0	0	1	0	0	0	2	0	1	0
25	4	1	tr	0	0	0	0	0	0	0	0	0	0	0	4	4	0
31	4	2	3	1	1	tr	1	tr	2	2	4	4	3	4	2	1	2
36	4	3	2	0	0	0	1	0	0	0	1	0	0	0	1	0	0
38	4	4	2	1	0	0	0	0	3	3	4	3	2	4	4	1	1
39	4	4	4	2	1	1	1	2	4	4	4	4	3	4	3	4	3
46	4	1	2	0	0	0	0	1	4	4	4	4	4	4	4	4	2
47	4	2	2	1	1	1	0	1	0	3	3	0	1	0	4	0	0
50	4	4	4	1	1	1	2	1	3	1	1	2	1	1	1	1	1
54	4	tr	4	0	0	0	0	0	0	4	3	0	4	4	0	0	4
63	4	4	4	2	1	0	0	0	1	1	1	1	1	2	2	1	1
71	4	4	1	0	0	0	0	0	0	0	0	0	0	1	4	0	0
1X10	4	0	4	0	0	0	0	1	0	0	0	0	0	2	3	0	4
11	4	1	2	0	0	tr	0	0	0	4	3	0	0	4	0	0	3
33	4	3	3	4	3	4	3	3	0	1	0	0	0	0	2	1	0
35	4	1	3	2	0	0	0	0	1	0	0	0	0	0	1	0	0
56	4	4	tr	tr	0	0	0	0	0	0	1	1	1	0	0	0	0
61	4	4	3	0	0	0	2	2	2	4	4	0	0	4	4	4	4
63	4	3	3	2	1	1	1	1	0	2	4	3	4	3	3	0	1
68	4	3	2	0	1	1	1	1	1	0	1	0	0	0	1	4	1
72	4	4	3	1	1	0	0	1	4	3	4	4	1	1	2	3	1

\* A turbidity value of 4 indicates heavy growth; lower values indicate correspondingly less growth.

Illustrative of the differences in specific nutritional requirements between organisms of the same group are results from a more detailed study of cultures of group IV, all requiring amino acids plus growth factors for maximum growth. Each culture was inoculated into 17 different media, including medium AG as control and two series of media, one with all amino acids plus single growth factors, and one with all growth factors plus single amino acids. From table 5 it is

seen that within the group there are wide differences in individual nutritional requirements. The results suggest that the indigenous soil bacteria may exercise highly specialized functions, such as the utilization of specific chemical compounds formed during the process of decomposition of organic matter. The variability brought out by more detailed study of related organisms further emphasizes the difficulty in classification of soil bacteria.

There is comparatively little exact knowledge of the occurrence of bacterial growth factors in soil. The presence of vitamins of the B group, most of which are important for the nutrition of many bacteria, is probable in soils receiving organic fertilizer. Sanborn (6) has shown that during the decomposition of plant material in soil, growth accessory factors for cellulose-decomposing bacteria may be elaborated. Lilly and Leonian (2) have demonstrated the presence of thiamin, and the occurrence of biotin in plant and animal tissue and in manure may well account for its presence in well-fertilized soils. Furthermore West (8) has shown that measurable quantities of thiamin and biotin may be excreted by the roots of seedlings.

Results from our studies with organisms requiring soil extract suggest the presence of other, probably unknown, microbial growth factors in soil. This group showed no growth with the nutilite supplement, which included thiamin, biotin, riboflavin, pyridoxin, pantothenic acid, nicotinic acid, and inositol, suggesting that the growth-promoting properties of soil extract for this group are to be ascribed to factors other than those named. Differences in response of certain organisms to extracts from different soils as well as to the nutilite effect of filtrates of other soil organisms appear to indicate the presence of more than one such growth-promoting factor in soil.

#### SUMMARY

Based on a determination of growth requirements, a classification was made of soil bacteria isolated by nonselective plating methods. Seven main nutritional groups were recognized, ranging from organisms capable of maximum development in a simple basal medium to types unable to develop with supplements of amino acids, growth factors, or yeast extract, but which require soil extract for growth. The more fertile soil of two studied showed a higher proportion of types with more complex growth requirements than the poorer soil.

More detailed study of the requirements of individual cultures of one group (requiring amino acids and growth factors) showed wide variations between related forms. The results suggest that many soil bacteria exercise functions of a highly specialized nature.

Correlation of nutritional requirements with morphological type did not reveal any clear-cut relationship, though certain trends were noted. Organisms with simpler requirements consisted to a larger extent of sporeforming rods and Gram-negative nonsporing rods. Pleomorphic forms related to corynebacteria comprised a greater proportion of organisms with more complex nutritional needs.

Bacteria requiring soil extract for growth comprised 19 per cent of the isolates

from soil. For the great majority of these forms, the growth-promoting properties of soil extract were dependent upon a factor or factors not concerned with the ash constituents, but present in the acetone extract and capable of adsorption by charcoal and of recovery by elution. Since the organisms showed no growth with a combination of seven known growth factors, it is suggested that the growth-promoting properties of soil extract for this group of bacteria are to be ascribed to factors other than these. Soils may vary greatly in the effectiveness of extracts prepared from them for certain organisms.

For certain organisms requiring soil extract, the nutritive effect of the latter could be replaced by a filtrate from cultures of other soil bacteria capable of maximum development in simple basal medium. For other organisms, similar filtrates were ineffective, indicating different growth requirements and suggesting that soil extract contains more than one growth-promoting factor.

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## BOOKS

*The Economics of Soil Conservation.* By ARTHUR C. BUNCE. The Iowa State College Press, Ames, 1942. Pp. 227, figs. 4. Price, \$3.

In this book a well-informed soil-minded economist considers the interrelationships between the technological and the economic problems involved in soil conservation as an objective of social planning. Of the 12 chapters, the following deserve special mention: the relationship of rent to the elasticity of production and intensity of land use; exploitation of virgin fertility and the intensive and extensive margins; price changes and conservation; the individual and fertility maintenance; the individual and conservation when exploitation induces erosion or soil deterioration; society and conservation; methods of soil control over land use; problems of measurement in conservation planning; war and conservation; the formulation of public policy and action. This highly instructive book merits a careful reading by every intelligent man who has anything whatever to do with the formulation of policies relating to soil conservation and land use.

*Field Crops.* By HOWARD C. RATHER. McGraw-Hill Book Company, Inc., New York, 1942. Pp. 454, illus. 130. Price, \$3.75.

A well-written and well-illustrated textbook dealing with the theory and practice of crop production, and with land management in relation thereto. Among the chapter headings are: soil conservation and management, tillage and cultivation, legumes for forage, haymaking, silage, pasture and pasture management, corn, wheat and rye, oats and barley, potatoes and sweet potatoes, cotton, tobacco, and crop improvement. One cannot but be impressed with the enormous amount of practical information required in the writing of this book.

*Field Crops and Land Use.* By JOSEPH F. COX AND LYMAN JACKSON. John Wiley and Sons Company, New York, 1942. Pp. 473, figs. 150. Price, \$3.75.

A comprehensive discussion of the problems involved in the production of the great variety of crops that are grown in the United States. The first third of the book is devoted to a consideration of crop adaptations, crop rotations, fertility maintenance, soil conservation, control of weeds and plant pests, and the use of cover crops; and the last two thirds, to the individual food, feed, and fiber crop plants. The illustrations are excellent. The book is dedicated to progressive farmers, and every such farmer should find it useful in planning his cropping program. In proportion as the war period lengthens and food needs increase, there will be greater need to reexamine our crop production plans to the end that full use be made of our land and labor resources. This book will be of help in that connection.

*Food for Thought.* By HERMAN FREDERICK WILLKIE AND PAUL JOHN KOLACHER. Indiana Farm Bureau, Inc., Indianapolis, 1942. Pp. 209, figs. 28. Price, \$2.

This book deals with the possible production of alcohol from unsalable portions of corn, small grains, sugar beets, potatoes, and sweet potatoes. Consideration is given to the technical aspects of the use of ethyl alcohol as a motor fuel, the possibilities in building community distilleries, the amounts of raw materials that would be required, the cost of producing them, and the development and design of a continuous cooking and mashing system and of a continuous process for the production of pure cultures of distiller's yeast. The point of view presented is that it is entirely feasible for farmers to produce their own farm fuel and that if this were done it would have a stabilizing influence on crop prices and indirectly on general business conditions. A highly instructive and interesting presentation of this problem.

*Geomorphology.* By O. D. VON ENGELN. The MacMillan Company, New York, 1942. Pp. 655, illus. 372. Price, \$4.50.

The title of this book suggests discourse on the form of the earth, but the contents include not only a discussion of land forms but of the form of the earth as a whole, and of its continents and oceans, as well. The book is of special interest to workers in the field of soil conservation in that it deals with the larger aspects of erosion by wind and water and lays the groundwork for a more detailed consideration of the effects of these two types of erosion on the soil itself. The illustrations are exceptionally clear-cut and instructive and emphasize the quotation from Tao Te Ching, 240 B.C., with which the author begins his discourse: "Nothing under heaven is softer or more yielding than water; but when it attacks things hard and resistant there is not one of them that can prevail."

*Handbook of Chemistry.* Fourth Edition. Compiled and edited by NORBERT ADOLPH LANGE. Handbook Publishers, Inc., Sandusky, Ohio. Pp. 1603, plus an appendix of 271 pages of mathematical tables and formulas, and an index of 35 pages. Price, \$6.

An exceptionally useful book containing information on a great variety of subjects beginning with first-aid measures for accidents and antidotes for poisons, and ending with the 200-year calendar. Of particular interest to those in the field of soil and plant science are the parts dealing with properties of minerals, the vitamins, electrometric determination of hydrogen-ion concentration, acid-base indicators, and laboratory solutions. Anyone in need of a ready reference book will find almost everything he requires in this volume.

*Life and Work of C. F. Marbut.* Prepared for publication by H. H. KRUSEKOPF. Soil Science Society of America, G. G. Pohlman, Sec.-Treas., Morgantown, West Virginia, 1942. Pp. 271. Price, \$2.

As the title indicates, this book is dedicated to the memory of Curtis Fletcher Marbut, professor of geology at the University of Missouri, 1895-1910, and soil scientist of the Bureau of Chemistry and Soils, U.S. Department of Agriculture, 1910-1935. Its purpose is to bring together Marbut's unpublished and less

accessible articles, along with interesting biographical material, and to evaluate his outstanding contributions to soil science. No specialist in this field can afford not to own a copy of this book for careful reading and ready reference.

*New Commercial Chemical Dictionary.* Compiled by ANTONIO PEROL GUERRERO. Chemical Publishing Co., Inc., Brooklyn, New York. Pp. 600. Price, \$10.

A Spanish-English and English-Spanish dictionary, including conversion tables of weights, measures, and monetary units. The need for this dictionary arises out of the rapid industrial development in the United States and its far-reaching effects on the Spanish-speaking countries to the south. Many of the technical and commercial words employed in the United States have no corresponding Spanish words. The dictionary attempts to set a standard of terminology for all such words and to that end has selected some 50,000 words for inclusion in this volume. The dictionary will be highly useful to those who are concerned in any manner with Central and South American relationships.

*The Peats of New Jersey and Their Utilization, Part A.* SELMAN A. WAKSMAN. Bulletin 55, Geological Series, Department of Conservation and Development of New Jersey. Pp. 155, figs. 18. Price, \$0.50.

A survey of the development of our knowledge of the nature, origin, composition, classification, and utilization of peats in this country and abroad. Attention is directed to the confusion of terms used to designate peats and peat formations. The reasons for this confusion are examined in detail. An attempt is made to simplify the concept of peat as a whole, and of the various peat types as produced in different regions from different plants and under different topographic and environmental conditions. The botanical and chemical criteria for the classification of peats are examined critically and evaluated. The relationships between available nutrients, plant associations, and peat formations are correlated. Four major and several minor types of peat are recognized.

*The Principles of Field Drainage.* By H. H. NICHOLSON, Cambridge University Press. The Macmillan Company, New York, 1942. Pp. 165, figs. 29. Price, \$3.

The material in this book is based on 10 years' study of field drainage problems in England and Wales, especially those of heavy soils. Of greatest interest is the chapter dealing with mole drainage, the history of which goes back some 200 years on the heavy clay soils of Great Britain, particularly those having very clayey subsoils. The essentials of this operation are the drawing of a metal mole through the soil at a depth between 15 and 24 inches, the resulting channels being spaced from 3 to 5 yards apart. The cost is estimated at about one tenth of that involved in draining land by the use of tile, and there appears to be little difference in the effectiveness of the two systems. Everyone concerned with field drainage will find this book of considerable interest and value.

*This Land We Defend.* By HUGH H. BENNETT AND WILLIAM C. PRYOR. Longmans, Green and Company, New York, 1942. Pp. 107, illus. 21. Price, \$1.50

A popular presentation of the problem of soil conservation and the methods by which erosion losses are brought under control. The full-page illustrations are photographic reproductions showing severely eroded areas before and after conservation practices were adopted. The book can easily be read in one evening and, as the wrapper suggests, should then be sent on to "some man in the Service who needs good reading."

*Ways of the Weather.* By W. J. HUMPHREYS. The Jacques Cattell Press, Lancaster, Pennsylvania, 1942. Pp. 400, figs. 44. Price, \$4.

This book is "one of the humanizing science series." It tells about the weather in a manner that is suited to the needs of most of us who want to know the facts without having to work too hard to get them. One has the impression from reading the book that the author enjoys the weather—the bad as well as the good. The illustrations are exceptionally well chosen, and the material is presented in a manner that is both factual and entertaining.

*Weed Control.* By WILFRED W. ROBBINS, ALDEN S. CRAFTS, AND RICHARD N. RAYNOR. McGraw-Hill Book Company, Inc., New York, 1942. Pp. 543, figs. 202. Price, \$5.

A timely new book dealing with the weed problem from its early beginning when introduced species spread westward with the population down to the present use of modern methods in weed control. Among the topics considered in the 16 chapters are: weeds and human affairs, reproduction, association with soils and crops, prevention of spread, principle of control, competition with crops, use of sprays, the application of chemicals for soil sterilization, including the chlorates, borates, arsenicals, and thiocyanates. A long list of up-to-date references is appended to each chapter.

THE EDITORS

# THE SALT INDEX—A MEASURE OF THE EFFECT OF FERTILIZERS ON THE CONCENTRATION OF THE SOIL SOLUTION<sup>1</sup>

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Germination of seeds may be prevented, or established crops may be injured by the presence of too much soluble salt in the soil. Such injury may occur even though all elements which the plant requires for its proper nutrition are present in the normal proportions to one another and substances that may exhibit specific plant toxicity effects, such as copper and zinc, are not present in excess. This type of injury must therefore be connected with the high concentration of the soil solution, and it has been commonly thought that the elevated osmotic pressure of such solutions is responsible for the injury. Most studies of the relation of the osmotic pressure to plant growth have been limited, however, to solution or sand cultures. Magistad and his co-workers, for example (3), have recently reported that growth reduction of several crops in sand cultures was linear with increasing osmotic pressure of the substrate over the range from 0.4 to 4.4 atmospheres and that a number of crop species died when the osmotic pressure of the culture solution reached 4.5 atmospheres. The presence of soil undoubtedly modifies the effect of the high salt content of the culture medium; nevertheless, the osmotic pressure of the soil solution must be an important factor in crop injury.

Except under unusual conditions the osmotic pressure of the soil solution should never become high enough to injure the crop when the fertilizer is uniformly broadcast. When the fertilizer is localized in a small zone, however, as in various special placements, the soluble portion of the fertilizer dissolves only in the soil moisture immediately surrounding that zone. This results in local areas of salt solution many times as concentrated as that met with in broadcast application, and not infrequently injury to plants follows if due precautions are not taken. Such injury can be prevented by locating the fertilizer zone farther from the row, by reducing the amount of fertilizer, and by reducing the tendency of the fertilizer to injure the plant. In general, if no plant injury intervenes, most efficient use of fertilizer will result when the zone is close to the row, as this place-

<sup>1</sup> A paper on the "Effect of Mixed Fertilizers and Fertilizer Materials on the Concentration of the Soil Solution" by the same authors and containing a portion of the material here presented, was given, as Paper No. 4, before the Division of Fertilizer Chemistry of the American Chemical Society at the 1942 Fall Meeting, Buffalo, New York, September 7 to 11, 1942.

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<sup>3</sup> Division of Soil and Fertilizer Investigations, Beltsville, Md. This study would hardly have been possible without the expert assistance of various members of the Soil Survey and Soil Conservation Service in locating and collecting the soil samples. The authors wish to express their appreciation of this service.

ment will ensure less consumption of fertilizer by weeds and the roots of the new seedling will quickly reach the fertilizer, a desirable feature in infertile soils where the plant might otherwise make a slow start. Reducing the amount of fertilizer to avoid injury might mean going below the optimum amount of plant food. The possibility of reducing the tendency of the fertilizer to injure plants, thereby making placement of the optimum amount in the best position more feasible, is thus worthy of consideration.

White and Ross (5) have shown how the effect of different fertilizers of the same grade on the concentration of the soil solution may vary widely in accordance with the materials used in their formulation. It is possible, for example, to formulate two mixed fertilizers of the same grade, such as 1-8-4, one of which will increase the osmotic pressure of the soil solution four times as much as the other when equal amounts are applied. Obviously the optimum placements for these two mixtures may be markedly different. Ross, Adams, and Rader (4) have recently shown that fertilizers having relatively little effect on the osmotic pressure of the soil solution gave better yields when placed in bands one-half inch from the seed than did the same amount of the same grade of a fertilizer producing large increases in the osmotic pressure when placed 2 inches from the seed. The latter fertilizer seriously reduced germination when applied at the rates used in this experiment and one-half inch from the seed. The materials used in the formulation of fertilizer mixtures differ with market conditions, with supply, and with other factors, and the mere statement of the grade is not sufficient to guarantee that the favorite grade of this year may not have a very different effect on the soil solution from the same grade of last year or the year before. Further discussion of these points is contained in the paper by White and Ross (5).

It would be possible to determine the effect of each individual fertilizer on each soil, but this is unnecessary, since it has been found possible to predict the effect of complete mixed fertilizers from a knowledge of the effect that their individual components have on the soil solution. The present paper gives the results of a study of the osmotic pressure produced in the soil solution by numerous fertilizer materials and shows how these data, by means of a new quantity called the "salt index," may be used to predict the relative effect of any mixed fertilizer the formula of which is known. A quantity called the "osmotic index number," designed for the same use, has been described by White.<sup>4</sup> The salt index proposed at this time differs from the osmotic index only in the choice of sodium nitrate as a reference material instead of ammonium sulfate. White's work was based on the limited data available in 1939, but the greatly extended data described in this paper confirm, in general, the conclusions drawn by White.

#### GENERAL METHOD

The osmotic pressure produced in the soil solution by a given salt application is the result of many factors. Among these may be mentioned the quantity of

<sup>4</sup> "The Relationship Between the Salt Index of a Fertilizer and Its Most Efficient Placement in the Soil," by Lawrence M. White. Unpublished paper given before the National Joint Committee on Fertilizer Application at its fifteenth meeting, held in New Orleans, November 21, 1939.

salt added, the amount of moisture in the soil, base exchange and other reactions into which the added salt may enter, the temperature, and the amount of biological action in the soil. Systematic investigation of the effect of all these variables is beyond the scope of the present study. Nevertheless it is possible to choose a set of conditions and by controlling these conditions to obtain reproducible results that may be considered as representing average circumstances.

The apparatus and method used in this work have been described in detail by White and Ross (5) and will be discussed here in outline only. The fertilizer or salt to be tested was mixed with the air-dried soil that had been previously passed through a 2-mm. sieve and thoroughly mixed. The soil was then sprayed with sufficient water to bring the moisture content to 75 per cent of its moisture equivalent, after which it was stored in a closed container for 5 days at about 5°C. This allows the soil and the added fertilizer to reach equilibrium or at least to arrive at a steady state where further change is very slow, and at the same time biological activity is reduced to a minimum. After 5 days the soil was allowed to come to room temperature and was then packed in the cylinder of the Burd-Martin apparatus (1) as described by White and Ross (5). So far as possible their exact technic was followed except that, with some soils, it was found necessary for best results to alter the degree of compaction. Conductivity and freezing point determinations were made immediately on the displaced soil solution. The freezing point lowering values were converted into osmotic pressure by means of the table of Harris and Gortner (2) with interpolation when necessary to give the osmotic pressure corresponding to each 0.001°C. In all subsequent discussion the expression "osmotic pressure" refers to the osmotic pressure so calculated. In computing acre applications of various materials the usual assumption was made that an acre of dry soil  $6\frac{3}{4}$  inches deep weighs 2,000,000 pounds. The total water-soluble salts in fertilizers were determined by extracting 1 gm. on a 9-cm. filter paper with 250 cc. of water at room temperature, drying and weighing the extracted salt.

#### MATERIALS

The soils studied are listed in table 1 with their sources, silt, clay, and organic matter contents, pH values, and moisture equivalents and the osmotic pressures of the soil solutions of the unfertilized soils. These osmotic pressure values constituted the blank determinations that were deducted from the total osmotic pressures to obtain the increases due to the added materials. These blanks were redetermined frequently as the work progressed, but only minor variations were observed. The values in table 1 are the averages of these determinations. The Hagerstown silty clay loam and the Chester clay loam were virgin soils. All others had been cultivated but not recently fertilized prior to sampling. The osmotic pressures of the soil solutions of the unfertilized soils were therefore relatively low, and these blanks were, in most cases, a small part of the total osmotic pressure measured. All soil samples were taken to a depth of 6 to 7 inches only, after all litter and vegetation had been removed. The clay and silt contents listed in table 1 show a wide range of values, indicative of great differences in texture and presumably in other soil properties.



Special fertilizer materials used in the osmotic pressure studies are listed in table 2. All these materials, except sulfate of potash-magnesia were prepared in

TABLE 1

*Sources, moisture equivalents, pH values, and silt, clay, and organic matter contents of soils studied, and osmotic pressures of soil solutions of the unfertilized soils\**

SOIL TYPES	LOCATION	MOISTURE EQUIVALENT	pH	OSMOTIC PRESSURE†	SILT 0.05-0.002 MM.	CLAY <0.002 MM.	ORGANIC MATTER‡
		<i>per cent</i>		<i>atm.</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Norfolk sand	Edgeville Co., South Carolina	5.1	5.4	0.349	10.6	4.2	0.1
Sassafras sandy loam	Gloucester Co., New Jersey	13.1	5.5	0.410	22.2	7.2	1.2
Hartsells silt loam	Cumberland Co., Tennessee	21.9	4.9	0.320	54.0	14.6	2.2
Cecil clay	Abbeville Co., South Carolina	26.3	4.9	0.070	22.1	41.3	0.2
Hagerstown clay	Washington Co., Maryland	27.7	7.6	0.390	41.5	43.2	0.3
Hagerstown silty clay loam	Washington Co., Maryland	31.6	7.0	0.428	76.9	12.9	0.8
Chester clay loam	Montgomery Co., Maryland	32.5	4.4	0.362	48.7	20.4	3.7

\* pH determinations by E. H. Bailey. Mechanical analyses and moisture equivalent determinations by E. F. Miles and T. M. Shaw.

† Osmotic pressure of the soil solution of the unfertilized soil.

‡ Organic matter dissolved by  $H_2O_2$ .

TABLE 2

*Percentage composition of special fertilizer materials used in salt index studies*

MATERIAL	K <sub>2</sub> O EQUIVALENT	KCl	NaCl	K <sub>2</sub> SO <sub>4</sub>	MgSO <sub>4</sub> ·7H <sub>2</sub> O	CaSO <sub>4</sub> ·2H <sub>2</sub> O	INSOLUBLE MATERIAL
Kainite.....	12.5	20.0	49.5		15.5	6.3	8.7
Kainite.....	17.5	28.0	44.8		15.5	6.3	5.4
Manure salts.....	20.0	32.0	42.5		15.5	6.3	3.7
Manure salts.....	30.0	48.0	21.3		15.5	6.3	8.9
Potassium chloride..	50.0	79.2	12.0		2.0*	1.0*	5.8
Potassium chloride..	60.0	95.0	5.0				
Sulfate of potash-magnesia.....	22.0		2.0	41.0	56.0*	1.0*	

\* Percentage of the anhydrous compound.

the laboratory to give the compositions indicated. These particular compositions were chosen because they approximate the average compositions of these materials indicated by numerous analyses recorded in the bulletins of various

state control laboratories.<sup>5</sup> The sulfate of potash-magnesia is the domestic product originating in the New Mexico potash fields.

The experimental mixed fertilizers prepared especially for this study are listed in table 3. These fertilizers were prepared chiefly from commercial materials, except as noted in footnotes. Fertilizers 1 to 6 inclusive, referred to in later tables, were prepared by White and Ross (5) and the data on them were furnished by those workers. Fertilizer 109, also referred to later, differs from

TABLE 3  
*Composition of experimental mixed fertilizers used in salt index studies*  
Pounds per ton

MATERIAL	6-8-4 NO. 101	6-8-4 NO. 102	6-8-4 NO. 103	6-8-4 NO. 104	9-12-6 NO. 105	9-12-6 NO. 106	9-12-6 NO. 107	9-12-6 NO. 108
Ammonia (anhydrous), 82.2 per cent N .....	30.0		24.0		36.0	30.0		
Ammonium sulfate, 20.9 per cent N..	143.5	191.3	143.5	191.3		287.1		191.4
Cal-Nitro*, 25.5 per cent N.....	78.4		78.4		19.6			
Potassium nitrate, 13.7 per cent N, 44.4 per cent K <sub>2</sub> O.....					270.2		231.9	
Sodium nitrate, 16.3 per cent N ...		490.7		490.7		428.4		464.0
Uramon, 42.1 per cent N.....	106.8		118.7		208.6	59.3	151.9	
Cottonseed meal, 6.9 per cent N..					289.9		434.8	144.9
Ammonium phosphate, 10.6 per cent N, 47.0 per cent P <sub>2</sub> O <sub>5</sub> .....							510.2	510.2
Superphosphate, 19.6 per cent P <sub>2</sub> O <sub>5</sub> ..	816.3	816.3	816.3	816.3				
Superphosphate, 48.5 per cent P <sub>2</sub> O <sub>5</sub> .					490.4	490.4		
Potassium chloride†, 57.2 per cent K <sub>2</sub> O.....	140.0	139.8					29.7	
Kainit†, 16.5 per cent K <sub>2</sub> O.....			484.9	457.1				
Manure salt‡, 29.8 per cent K <sub>2</sub> O...						402.1		402.1
Dolomite.....	286.0	100.0	286.0	44.6	174.2	284.7	392.5	287.4
Sand.....	399.0	261.9	48.2		511.1	18.0	249.0	

\* 74 per cent NH<sub>4</sub>NO<sub>3</sub> and 26 per cent dolomite.

† Partial index number for one unit = 2.007 by interpolation between 50 and 60 per cent KCl.

‡ 30.62 per cent KCl + 40 per cent calcined kieserite + 29.38 per cent NaCl.

§ 45 per cent KCl + 45 per cent NaCl + 10 per cent dolomite.

fertilizer 108 only in the use of sand instead of dolomite to fill out the formula. Number 109 is therefore essentially a calcium-free fertilizer. Low, medium, and high analysis mixtures were included in those studied, and the pairs 2 and 3, 105 and 106, and 107 and 108 were designed to show very low and very high effects on the osmotic pressure of the soil solution by fertilizers of the same analysis. The commercial fertilizers studied are listed in table 4. These also are of varying analysis, and, as shown later, vary more than twofold in their effect on the osmotic pressure of the soil solution.

<sup>5</sup> Private communication from A. L. Mehring.

TABLE 4  
*Composition of commercial mixed fertilizers used in salt index studies*  
 Pounds per ton

	8-24-8 NO. 9	8-24-8	8-16-16 NO. 11	8-16-16 NO. 12	8-12-20 NO. 13	8-12-20 NO. 14	12-16-12 NO. 15	12-16-12 NO. 16	NO. 17	4-12-4 NO. 18
Ammonium sulfate, 20.0 per cent N. ....									228	
Ammonium sulfate, 21.0 per cent N. ....			270	245	350	320	300	146		150
Cyanamid, 22.0 per cent N. ....									60	60
Cyanamid, 21.0 per cent N. ....									20	70
Potassium nitrate, 13.0 per cent N, 42.5 per cent K <sub>2</sub> O. ....			120		170					
Sodium nitrate, 16.3 per cent N. ....									100	100
Sodium nitrate, 16.5 per cent N. ....	260									
Urea, 46.6 per cent N. .		152		87		87		300		
UAL-B, 45.3 per cent N. ....		198				120		157		
Nitrogen solution 4, 37.0 per cent N. ....	170		240	157	180		100			
Garbage tankage. ....									100	
Cocoa meal. ....									100	
Agrinite. ....										100
Ammonium phos- phate, 11.0 per cent N, 48.0 per cent P <sub>2</sub> O <sub>5</sub> . ....	530						390*			
Superphosphate, 18.0 per cent P <sub>2</sub> O <sub>5</sub> . ....									890	1325
Superphosphate, 45.2 per cent P <sub>2</sub> O <sub>5</sub> . ....	510	1043	710	710	530	530	300	710		
Potassium chloride, 60.0 per cent K <sub>2</sub> O. .	270	270	450	540	550	670	60	400	164	135
Calcined kieserite, 33.5 per cent MgO. .			110		110					
Conditioner. ....	100	150	100	100	110	163	210	100		
Dolomite. ....	160	187		161		110	160	187	338	60

\* Ammo-Phos B, 20.0 per cent N, 49.0 per cent P<sub>2</sub>O<sub>5</sub>.

#### OSMOTIC PRESSURE INCREASES DUE TO SINGLE FERTILIZER MATERIALS

All together, about 45 single fertilizer materials were studied for their effect on the osmotic pressure of the soil solution of Norfolk sand. Many of these were also studied on six other soils, and several were studied at varying rates of application on the various soils but especially on the Norfolk and Cecil soils. Only data necessary to the discussion are presented here, in tables 5 and 6. Some

TABLE 5

*Increase in osmotic pressure of soil solutions of several soils due to varying applications of fertilizer materials*

MATERIAL	lbs./A.	NUTRI- ENT*	INCREASE IN OSMOTIC PRESSURE OF SOIL SOLUTIONS						
			Nor- folk sand	Sassa- fras sandy loam	Hart- sells silt loam	Cecil clay	Hagers- town clay	Hagers- town silty clay loam	Chester clay loam
		lbs./A.	atm.	atm.	atm.	atm.	atm.	atm.	atm.
Ammonium sulfate.....	377	80	1.508			0.063	0.309		
	1000	212		1.411	0.717	0.352	0.510	0.590	0.290
	1509	320	6.161			0.484	0.816		
	2000	424	8.251	2.332	1.706	0.883	0.791	0.690	1.039
	3019	640	12.161	3.531	2.536	1.739	1.141	1.590	1.620
Ammonium nitrate.....	228	80	1.218			0.084			
	914	320	5.391			0.494			
	1828	640	11.322			1.141			
Sodium nitrate.....	485	80	2.942			0.376	0.707		0.030
	1942	320	11.235			1.714	2.274		1.201
	2000	330	11.919	4.893	2.675	1.884	2.551	2.074	2.122
	3884	640	22.911			3.498	4.418		2.763
Cottonseed meal.....	571	40	0.121			0.000			
	2286	160	0.615			0.048			
	4572	320	1.375			0.157			
Monoammonium phosphate..	259	160	0.109			0.026	0.116		0.000
	1037	640	1.062			0.063			0.074
	2000	1234	4.038	0.518	0.295	0.169	0.020	0.114	0.315
	2075	1280	3.532			0.255	0.261		0.206
Potassium chloride.....	127	80	0.724			0.051	0.285		0.120
	507	320	2.930			0.171	0.695		0.330
	1013	640	6.566			0.678	1.455		0.850
	2000	1260	13.491	5.212	2.790	1.485	2.515	2.140	1.955
Kainite (12.5 per cent K <sub>2</sub> O) ..	640	80	3.966						
	1280	160	7.866						
	2560	320	15.939						
Superphosphate (18.6 per cent P <sub>2</sub> O <sub>5</sub> ).....	860	160	0.844			0.084			
	3440	640	1.122			0.531			
	6880	1280	1.725			0.977			

\* "Nutrient" refers to nitrogen (N) in the nitrogen carriers, to potash (K<sub>2</sub>O) in the potash carriers, and to phosphorus (P<sub>2</sub>O<sub>5</sub>) in the phosphorus carriers.

of the materials studied are not ordinarily used directly in fertilizers but were included because they may occur incidentally in fertilizer materials, such as sodium chloride in manure salts, or may be formed as the result of reactions

TABLE 6  
Data for calculating salt indexes of mixed fertilizers

MATERIAL	ANALYSIS*	INCREASE IN OSMOTIC PRESSURE†	MATERIAL PER UNIT PLANT FOOD	SALT INDEX‡	FACTOR§	PARTIAL INDEX NUMBER
	per cent	atm.	wt.			
<i>Nitrogen carriers</i>						
Ammonia**	82.2	.2776	0.243	47.1	2.352	0.572
Ammonium acid carbonate**	17.7	.0370	1.130	6.3	0.314	0.354
Ammonium nitrate**	35.0	.6180	0.571	104.7	5.237	2.990
Ammo-Phos A	11.0	.1585	1.818	26.9	1.343	2.442
Ammo-Phos B	20.8	.1840	0.962	31.2	1.559	1.500
Monoammonium phosphate**	12.2	.1766	1.639	29.9	1.497	2.453
Diammonium phosphate**	21.2	.2020	0.943	34.2	1.712	1.614
Ammonium sulfate**	21.2	.4070	0.943	69.0	3.449	3.253
Calcium nitrate** (4H <sub>2</sub> O)††	11.9	.3095	1.681	52.5	2.623	4.409
Cal-Nitro	20.5	.3605	0.976	61.1	3.055	2.982
Cyanamid	21.0	.1830	0.952	31.0	1.551	1.476
Nitrogen solution 2A	40.6	.4619	0.493	78.3	3.915	1.930
Nitrogen solution 3	40.8	.4152	0.490	70.4	3.519	1.724
Nitrogen solution 4	37.0	.4589	0.541	77.8	3.889	2.104
Organic ammoniates	3.0	.0207	6.667	3.5	0.175	1.169
Organic ammoniates	5.0	.0207	4.000	3.5	0.175	0.702
Organic ammoniates	7.0	.0207	2.857	3.5	0.175	0.501
Organic ammoniates	9.0	.0207	2.222	3.5	0.175	0.390
Organic ammoniates	11.0	.0207	1.818	3.5	0.175	0.319
Organic ammoniates	13.0	.0207	1.538	3.5	0.175	0.270
Potassium nitrate**	13.8	.4345	1.449	73.6	3.682	5.336
Sodium nitrate**	16.5	.5900	1.212	100.0	5.000	6.060
Uramon	42.0	.3915	0.476	66.4	3.318	1.579
Urea**	46.6	.4450	0.429	75.4	3.771	1.618
Urea-ammonia liquor 37	37.1	.1563	0.539	26.5	1.325	0.714
Urea-ammonia liquor A	45.4	.2463	0.441	41.7	2.087	0.920
Urea-ammonia liquor B	45.3	.2774	0.442	47.0	2.351	1.039
<i>Phosphate carriers</i>						
Ammo-Phos A	48.0	.1585	0.417	26.9	1.343	0.560
Ammo-Phos B	49.0	.1840	0.408	31.2	1.559	0.636
Monoammonium phosphate**	61.7	.1766	0.324	29.9	1.497	0.485
Diammonium phosphate**	53.8	.2020	0.372	34.2	1.712	0.637
Monocalcium phosphate** (H <sub>2</sub> O)††	56.3	.0911	0.355	15.4	0.772	0.274

\* By "analysis" is meant the percentage of N in nitrogen carriers, of P<sub>2</sub>O<sub>5</sub> in phosphate carriers, of K<sub>2</sub>O in potash carriers, of MgO in magnesium carriers including dolomite, of CaO in calcium carbonate and gypsum, and of Na<sub>2</sub>O in sodium chloride and sulfate.

† Produced in soil solution by 100 pounds of material per acre.

‡ Ratio of increase in osmotic pressure produced by material to that produced by same weight of sodium nitrate, based on salt index of 100.

§ Salt index divided by 20.

|| Salt index per unit of plant food supplied.

\*\* Chemically pure.

†† Water of crystallization.

TABLE 6—*Continued*

MATERIAL	ANALYSIS*	INCREASE IN OSMOTIC PRESSURE†	MATERIAL PER UNIT PLANT FOOD	SALT INDEX‡	FACTOR§	PARTIAL INDEX NUMBER
	<i>per cent</i>	<i>atm.</i>	<i>cent.</i>			
<i>Phosphate carriers—Continued</i>						
Monopotassium phosphate**.....	52.2	.0495	0.383	8.4	0.420	0.161
Monosodium phosphate**(H <sub>2</sub> O)††.	51.4	.2133	0.389	36.2	1.808	0.703
Dimagnesium phosphate** (3H <sub>2</sub> O)††.....	40.7	.0254	0.491	4.3	0.215	0.106
Superphosphate.....	16.0	.0460	1.250	7.8	0.390	0.487
Superphosphate.....	18.0	.0460	1.111	7.8	0.390	0.433
Superphosphate.....	20.0	.0460	1.000	7.8	0.390	0.390
Superphosphate.....	45.0	.0595	0.444	10.1	0.504	0.224
Superphosphate.....	48.0	.0595	0.417	10.1	0.504	0.210
<i>Potash carriers</i>						
Kainit.....	12.5	.6250	1.600	105.9	5.297	8.475
Kainit.....	17.5	.6455	1.143	109.4	5.470	6.253
Manure salts.....	20.0	.6650	1.000	112.7	5.636	5.636
Manure salts.....	30.0	.5425	0.667	91.9	4.598	3.067
Potassium chloride.....	50.0	.6457	0.400	109.4	5.472	2.189
Potassium chloride.....	60.0	.6860	0.333	116.3	5.814	1.936
Potassium chloride**.....	63.2	.6745	0.317	114.3	5.716	1.812
Potassium nitrate**.....	46.6	.4345	0.429	73.6	3.682	1.580
Monopotassium phosphate**.....	34.6	.0495	0.578	8.4	0.420	0.242
Potassium sulfate**.....	54.0	.2720	0.370	46.1	2.305	0.853
Sulfate of potash-magnesia.....	21.9	.2548	0.913	43.2	2.159	1.971
<i>Miscellaneous</i>						
Calcium carbonate**.....	56.0	.0275	0.357	4.7	0.233	0.083
Calcined kieserite.....	33.5	.2285	0.597	38.7	1.936	1.156
Dolomite.....	20.0	.0049	1.000	0.8	0.042	0.042
Epsom salts**.....	16.4	.2595	1.222	44.0	2.199	2.687
Dimagnesium phosphate** (3H <sub>2</sub> O)††.....	23.1	.0254	0.866	4.3	0.215	0.186
Gypsum**.....	32.6	.0475	0.613	8.1	0.403	0.247
Magnesium oxide**.....	100.0	.0100	0.020	1.7	0.085	0.002
Sodium chloride**.....	53.0	.9075	0.377	153.8	7.691	2.899
Sodium sulfate**.....	43.6	.4375	0.458	74.2	3.708	1.698

that take place in the mixed fertilizer or in the soil, such as magnesium phosphate from the reaction of dolomite with superphosphate. Data on this class of materials permit the calculation of the probable osmotic pressure produced by reaction products or by mixtures known to contain these materials. For example, the effect of various grades of manure salts can be predicted if their content of sodium chloride and potassium chloride is known.

Inspection of table 6 shows that the low analysis potassium carriers such as 12.5 per cent kainit, and manure salts, and the inorganic nitrogen carriers such as sodium nitrate and ammonium sulfate produce the greatest increase in the osmotic pressure of the soil solution per unit of plant food. Phosphate carriers,

organic ammoniates, urea, ammonia, and the less soluble magnesium carriers have relatively little effect on the osmotic pressure of the soil solution.

#### THE SALT INDEX

If the effect of each fertilizer or fertilizer material on the osmotic pressure of the soil solution is taken relative to the effect produced by some standard reference material, a set of relationships are obtained that hold, within limits, for all the mixed fertilizers and soils studied. For this purpose it is proposed that sodium nitrate be taken as the reference material and that the salt index be defined as the ratio of the increase in osmotic pressure produced by the material to that produced by the same weight of sodium nitrate and, to give whole numbers, multiplied by 100. This relationship may be expressed by the following equation:

$$\text{Salt index} = \frac{100p}{p'}$$

where  $p$  = increase in osmotic pressure of the soil solution due to application of a definite weight of a fertilizer mixture or fertilizer material, and  $p'$  = increase due to application of the same weight of sodium nitrate under identical conditions.

It should be noted that the salt index does not predict the exact amount of fertilizer that will produce injury on a particular soil, but it does classify the fertilizer with respect to others as regards osmotic effect and shows which fertilizers will be most likely to injure crops. The salt index scale is so arranged that the effect of sodium nitrate is given the value 100 with the effects of other materials expressed relative to 100.

Fortunately the osmotic pressure usually increases in the Norfolk soil at a rate directly proportional to the amounts of material added to the soil when these amounts are within the normal range of fertilizer applications. Thus the ratio of the effect of ammonium sulfate to that of sodium nitrate, for example, is the same whether taken at 100 or 2000 pounds per acre. These relationships are shown in the several figures of the paper by White and Ross (5) and are further confirmed by the data of table 5 and by other data not reported here in detail. For some of the few materials, especially the phosphates, where the relation between amount applied and osmotic pressure is not strictly linear, the ratio, whenever possible, was taken in the range of the amounts of material normally used. Small errors so introduced probably do not have a significant effect on the result, especially since the phosphates have relatively little effect on the osmotic pressure of the soil solution. In considering the rate data of table 5, one should remember that Norfolk sand, with its low moisture equivalent and consequently relatively high osmotic pressure in the soil solution for a given application of material, presents by far the most favorable case for accurate results of the sort described in this paper. The other soils, especially those with the higher moisture equivalents, gave such low freezing point depressions that the experimental error sometimes amounted to a large fraction of the result. Furthermore, when these results are plotted, as was done by White and Ross for Cecil clay loam, the magnified osmotic pressure scale necessary makes curva-

tures that would scarcely be apparent on the Norfolk soil seem very large on the soils with higher moisture equivalents.

#### COMPUTING THE SALT INDEX OF A MIXED FERTILIZER

Data and factors useful in calculating the salt index of a mixed fertilizer are assembled in table 6. The first and second columns of the table list respectively most of the substances occurring in mixed fertilizers and their content of plant food<sup>6</sup> expressed as N,  $P_2O_5$ , or  $K_2O$  or as indicated in the footnotes. The third column gives the osmotic pressure increase in atmospheres produced per hundredweight of the material per acre in the soil solution of Norfolk sand under the conditions of this study. These values were computed from larger applications, usually 1 ton per acre. The fourth column lists the number of hundredweights of material necessary to supply one unit of the plant food in question. The salt indexes of the various fertilizer materials on the basis of sodium nitrate as 100 are listed in the fifth column. This permits the effect of any material, relative to that of sodium nitrate to be seen at a glance. The factor given in the sixth column is the salt index divided by 20. Since 20 pounds, 1 per cent of a ton, is the unit commonly used in fertilizer calculations, the use of this quantity introduces certain simplifications when calculating the salt index of a mixed fertilizer. The last column gives the "partial index number" or the salt index per unit of plant food supplied by each material. The partial index number is the product of the factor and the number of hundredweights of material required to supply a unit of plant food. The figures in the various columns are given to sufficient decimals to ensure that salt indexes of mixed fertilizers calculated from them will be correct to within one unit in the tenths place so far as the calculation is concerned.

When the number of units of plant food supplied by each component of a mixed fertilizer is known, the salt index of the mixed fertilizer is easily calculated by multiplying the partial index number for a unit, from table 6, by the number of units of plant food supplied by the material and adding the values so obtained. This is illustrated in the following example:

MATERIAL	ANALYSIS	LBS./TON	UNITS OF PLANT FOOD	PARTIAL INDEX NUMBER PER UNIT	PARTIAL INDEX NUMBER FOR UNITS USED
	<i>per cent</i>				
Ammonia.....	82.2	24.3	1	0.572	0.6
Urea.....	46.6	64.4	1.5	1.618	2.4
Sodium nitrate .....	16.3	61.3	0.5	6.060	3.0
Cottonseed meal.....	6.9	289.9	1	0.501	0.5
Superphosphate.....	20.0	1200.0	12	0.390	4.7
Calcined kieserite.....	33.5	59.7	1 (MgO)	1.156	1.2
Muriate.....	60.0	133.3	4	1.936	7.8
Dolomite.....	20.0	167.1	1 + (MgO)	0.042	0.1
Total.....		2000.0	Salt index.....		20.3

<sup>6</sup> The expression "plant food" is used in this paper in the sense that is commonly intended in the fertilizer industry; namely, the content of N,  $P_2O_5$ , or  $K_2O$  or of all three, in



When the number of units of plant food has not been calculated, the values in the last column are readily obtained by multiplying the number of hundredweights of material by the factor for that material. Thus the above mixture contains 1.333 hundredweights of 60 per cent muriate, which when multiplied by 5.814, the factor for this material, gives 7.8, the partial index number in the last column. If it is desired to know the actual effect of the fertilizer on the osmotic pressure of the soil solution of Norfolk sand or similar soil the osmotic pressures per 100 pounds of material from column three of table 6 are simply multiplied by the number of hundredweights of the corresponding material and the products added. The salt index is then obtained by dividing the total osmotic pressure by that produced by the same amount of sodium nitrate (11.80 atmospheres for a ton) and multiplying by 100. Materials such as mono-ammonium phosphate that contain two plant foods are listed in the two sections of table 6, corresponding to the two plant foods. This material, for example, is listed under both nitrogen carriers and phosphate carriers. In computing the salt index of a mixture the partial index number of such a material may be taken from either section but not from both.

The data in table 6 are based on the freezing point lowering determinations with some simplifications and adjustments where these seemed justified or necessary. These adjustments will not be discussed in detail, but some of the more important features of the table will be indicated. The organic ammoniates, per ton of material applied, all gave roughly the same small increase in osmotic pressure regardless of whether the actual material was fish scrap, dried blood, or other material. Since the effect of such material is small, no important error is introduced by taking them all as having the same effect, per ton of material, on the osmotic pressure. The effect per unit of plant food varies, however, with the analysis of the ammoniate. The data of table 6 can be applied without serious error to the animal organics including fish, horn, bone, and blood meals; to the vegetable organics such as seed, chaff, and hull meal and pomices; to leather, hair, hide, and other scrap included in process tankage; and to various sewage sludge products such as Milorganite, Nitrobac, and Nitroganic.

Similarly the ordinary and double strength superphosphates of slightly varying analysis are each lumped together in a group with the same salt index for all members of each group but with small differences in the partial index numbers. In general small variations in the analysis of a material, such as a few tenths of a per cent, can be ignored, especially if the material is one that has but little effect on the osmotic pressure. In the case of manure salts and kainite, which are frequently used in mixed fertilizers in large amounts and which increase the osmotic pressure very strongly, some adjustment of the values of table 6 should be made for analyses and compositions that do not fall close to those actually studied (table 2). The diluting materials in these potash salts are usually sodium chloride, calcium sulfate, magnesium sulfate, etc., and by use of the data for these materials, corrected values for the potash salt can be obtained if its composition is approximately known. Thus experimental mixed fertilizer No. 103 contained 484.9 pounds of 16.5 per cent kainit which consisted

of 148.5 pounds of potassium chloride, 194.0 pounds of calcined kieserite, and 142.5 pounds of sodium chloride. Reference to table 6 shows that these materials have factors of 5.716, 1.937, and 7.691 respectively; by multiplication, the partial index numbers for the amounts actually present are found to be 8.5, 3.8, and 11.0 respectively. The sum of these, 23.3, is the partial index number of the 484.9 pounds of kainit. Other difficulties can be resolved by similar methods.

#### VALIDITY OF CALCULATED SALT INDEX OF MIXED FERTILIZER

As a test of the validity of the calculation of the salt index of a mixed fertilizer from the indexes of its components, the actual osmotic effects of several experimental mixed fertilizers were determined in the laboratory on Norfolk sand. All fertilizer applications were at the rate of 1 ton per acre. The salt index values were obtained by dividing the osmotic pressure increase produced by the fertilizer by that produced by a ton of sodium nitrate on the same soil. Table 7 shows that these indexes so determined agreed well with the indexes computed by summing up the partial indexes of the components of each mixture. Similarly 10 commercial fertilizers were run on the Norfolk soil and the determined salt indexes compared with those calculated from the components of the mixtures. Table 7 shows that the agreement is satisfactory, though not so close as in the case of the experimental mixed fertilizers. The difference is probably due, in part, to lack of exact knowledge of the composition of the commercial fertilizers. These experiments with both the experimental and commercial mixed fertilizers confirm the feasibility of calculating the salt indexes of mixtures from the osmotic effects of the components of the mixtures.

As a further test of the validity of the salt index determined on the Norfolk soil when applied to other soils, the osmotic effects of fertilizers 101 to 108 inclusive were determined on six other soils and the salt index numbers calculated from the effect of sodium nitrate on the same soil. Table 8 shows that the indexes of mixed fertilizers determined on the Norfolk soil approximate those determined on the other soils studied, despite widely varying moisture, silt, and clay contents of these soils. This illustrates the convenience of using the salt index as a measure of the relative tendency of a fertilizer to injure crops rather than actual osmotic pressure values that vary widely with the soil studied. The salt index arranges fertilizers in the order of their increasing effect on the osmotic pressure of the soil solution and enables one to predict which fertilizer will be the most likely to injure crops through undue increase in the osmotic pressure.

Crops grown on sandy soils similar to the Norfolk are probably much more liable to injury through excessive osmotic pressure of the soil solution than are those grown on the heavier soils of higher moisture-holding capacity, simply because more osmotic pressure is produced by a given fertilizer application on the soil containing less moisture. It is thus apparent that the salt index of fertilizers should find its greatest application in connection with the management of the more sandy soils. Fortunately on the sandy soils it gives the most accu-

TABLE 7

*Comparison of salt indexes of mixed fertilizers determined on Norfolk sand with corresponding indexes calculated from osmotic effects of the fertilizer components\**

NUMBER	GRADE	SALT INDEX	
		Found	Calculated
<i>Experimental mixed fertilizers</i>			
1	3-10-5	20.9	20.3
2	6-20-10	34.6	37.4
3	6-20-10	90.1	89.2
4	3- 8-4	41.9	42.1
5	6- 8-4	24.5	24.5
6	6-16-8	29.6	30.8
101	6- 8-4	24.7	23.4
102	6- 8-4	41.9	41.8
103	6- 8-4	38.9	38.9
104	6- 8-4	55.6	55.6
105	9-12-6	22.6	20.5
106	9-12-6	64.2	60.6
107	9-12-6	21.2	22.8
108	9-12-6	63.3	63.9
109	9-12-6	61.9	63.8
<i>Commercial mixed fertilizers</i>			
9	8-24-8	43.3	45.1
10	8-24-8	28.4	31.5
11	8-16-16	54.2	54.6
12	8-16-16	48.9	50.5
13	8-12-20	60.4	61.7
14	8-12-20	57.0	58.1
15	12-16-12	44.7	41.7
16	12-16-12	45.3	46.4
17	4- 8-5	26.4	27.4
18	4-12-4	26.0	25.4

\* For composition of fertilizers 1 to 6 see White and Ross (5); for others, see tables 3 and 4.

TABLE 8

*Determined salt indexes of nine experimental mixed fertilizers on several soils*

FERTILIZER NUMBER	NORFOLK SAND	SASSAPRAS SANDY LOAM	HARTSELLS SILT LOAM	CECIL CLAY	HAGERSTOWN CLAY	HAGERSTOWN SILTY CLAY LOAM	CHESTER CLAY LOAM
101	24.7	24.7	22.4	25.4	23.3	24.2	21.2
102	41.9	42.3	45.1	47.0	42.9	35.7	39.2
103	38.9	37.4	37.7	44.2	37.1	33.8	33.5
104	55.6	56.9	53.7	61.3	53.1	57.0	53.8
105	22.6	13.9	17.5	17.1	18.4	15.0	18.4
106	64.2	59.5	54.9	58.6	51.4	54.6	54.7
107	21.2	14.7	18.7	23.2	21.6	14.0	19.8
108	63.3	57.5	57.8	58.0	55.1	52.2	54.7
109	61.9	59.9	57.1	56.4	55.1	52.2	58.0

rate predictions of the effect of the fertilizer on the osmotic pressure of the soil solution. It was largely because of these considerations that a typical sandy soil, the Norfolk, was chosen for most intensive study.

#### EFFECT OF VARYING SOIL MOISTURE ON OSMOTIC PRESSURE INCREASES

One of the chief factors governing the osmotic pressure produced in the soil solution by a given material is the water content of the soil. Other factors, such as varying colloid content and type of colloid, are also important, but these factors are closely related to moisture equivalent and thus the water content varies with them. Because of the very large effect of the soil moisture, therefore, it might appear that the osmotic pressure of the soil solution could be predicted with sufficient accuracy from the osmotic pressure produced by the fertilizer or fertilizer material when dissolved, in the absence of soil, in the amount of water corresponding to that contained in the soil in question. If this were not accurate enough there is still the further possibility of calculating the osmotic pressure of a soil solution of a particular soil from values determined on another soil by the simple process of adjusting the osmotic pressure values for the differences in solution concentration indicated by the moisture equivalents of the two soils. These two possibilities will be considered briefly.

Table 9, in the columns headed "soil solution," shows the osmotic pressure produced in soil solutions of several soils by ton-per-acre applications of six fertilizer salts and of nine mixed fertilizers. These are compared, in the columns headed "water only," with the osmotic pressures found when these materials were dissolved in the amounts of water corresponding to the moisture in the soils in question. Of the six salts, only sodium nitrate gave osmotic pressures approaching those found in the absence of soil. Ammonium sulfate and potassium chloride gave about 30 to 80 per cent of the pressure found in water solution in the absence of soil, whereas the phosphates, especially those of ammonium and calcium, gave only very small fractions of the water-solution values. Part of these observations are explainable in terms of known soil phenomena, such as phosphate fixation and base exchange, but discussion of such action will not be attempted at this time. The mixed fertilizers behaved similarly. In contact with the soil, many of them gave less than 50 per cent of the osmotic pressure found in the absence of soil. Prediction of the osmotic pressure of soil solutions from that of water solutions is therefore not feasible for any of the materials studied except possibly sodium nitrate.

Table 9 also shows, in the columns headed "calculated in soil solution," the osmotic pressure increases produced in Norfolk sand corrected for the amount of dilution indicated by the moisture contents of the other soils. This type of calculation should tend to compensate for the effect of colloid and other factors present in varying degrees in all soils. In fact, this method does give values in better agreement with the determined values for both single salts and mixed fertilizers than does the determination in water solution in the absence of soil. Wide differences are still found, however, in both groups. These variations are the expression of the complex reactions taking place between soil compo-

TABLE 9

*Osmotic pressure increases in Norfolk sand calculated to moisture content of other soils\* and compared with values determined in the soil solutions and in the corresponding amounts of water in the absence of soil*

All materials applied at rate of 1 ton per acre. Osmotic pressures expressed in atmospheres

FERTILIZER	NORFOLK SAND			SASSAFRAS SANDY LOAM			HARTSELLS SILT LOAM			CECIL CLAY			HAGERSTOWN CLAY			HAGERSTOWN SILTY CLAY LOAM			CHESTER CLAY LOAM		
	Dctd. on:		Calcd. in soil soln.	Dctd. on:		Calcd. in soil soln.	Dctd. on:		Calcd. in soil soln.	Dctd. on:		Calcd. in soil soln.	Dctd. on:		Calcd. in soil soln.	Dctd. on:		Calcd. in soil soln.	Dctd. on:		Calcd. in soil soln.
	Soil soln.	Water only		Soil soln.	Water only		Soil soln.	Water only		Soil soln.	Water only		Soil soln.	Water only		Soil soln.	Water only		Soil soln.	Water only	
<i>Fertilizer materials</i>																					
Ammonium sulfate.....	8.14	10.38	2.33	4.59	3.16	1.71	2.89	1.89	0.88	2.54	1.53	0.87	2.40	1.50	0.69	2.24	1.31	1.04	2.27	1.28	
Sodium nitrate.....	11.92	12.38	4.80	5.16	4.63	3.16	2.77	1.88	2.00	2.31	2.55	2.52	2.19	2.07	2.07	2.27	1.92	2.12	2.12	1.87	
Potassium chloride.....	13.49	14.30	5.22	5.90	5.24	2.79	3.54	3.14	1.49	2.97	2.01	2.52	2.88	2.48	2.14	2.62	2.17	1.96	2.44	2.11	
Monosodium phosphate.....	4.04	9.21	0.52	4.27	1.57	0.30	2.54	0.94	0.17	2.33	0.78	0.02	2.29	0.74	0.11	1.93	0.65	0.32	1.87	0.63	
Monocalcium phosphate monohydrate.....	1.82	5.28	0.05	2.45	0.71	0.19	1.44	0.42	0.10	1.25	0.35	0.01	1.22	0.33	0.00	0.93	0.29	0.00	1.12	0.29	
Monosodium phosphate monohydrate.....	4.27	8.81	0.72	3.77	1.66	0.52	2.18	0.99	0.35	1.88	0.83	0.23	1.87	0.78	0.12	1.65	0.69	0.42	1.48	0.67	
<i>Mixed fertilizers</i>																					
No. 101.....	2.92	4.22	1.21	2.52	1.14	0.60	1.12	0.68	0.46	0.95	0.57	0.57	1.04	0.54	0.50	0.83	0.47	0.45	0.88	0.46	
No. 102.....	4.94	5.90	2.07	2.65	1.92	1.21	1.57	1.15	0.85	1.36	0.96	1.05	1.28	0.91	0.74	1.24	0.80	0.83	1.16	0.78	
No. 103.....	4.59	5.40	1.82	2.39	1.79	1.01	1.45	1.07	0.80	1.30	0.89	0.91	1.21	0.84	0.70	1.07	0.74	0.71	1.10	0.72	
No. 104.....	6.56	7.76	2.78	3.19	2.56	1.44	1.88	1.53	1.11	1.78	1.27	1.30	1.62	1.21	1.18	1.46	1.06	1.14	1.44	1.03	
No. 105.....	2.67	4.26	0.68	1.78	1.04	0.47	0.97	0.62	0.31	0.99	0.52	0.45	0.87	0.49	0.31	0.76	0.43	0.39	0.74	0.42	
No. 106.....	7.57	8.59	2.91	3.72	2.93	1.47	2.15	1.77	1.06	1.87	1.47	1.26	1.80	1.39	1.13	1.59	1.22	1.16	1.52	1.19	
No. 107.....	2.50	4.44	0.72	1.92	0.97	0.50	1.00	0.58	0.42	1.01	0.49	0.53	0.88	0.46	0.29	0.90	0.40	0.42	0.75	0.39	
No. 108.....	7.47	9.26	2.81	3.89	2.91	1.55	2.28	1.74	1.05	2.04	1.45	1.35	1.92	1.37	1.08	1.68	1.21	1.16	1.64	1.17	
No. 109.....	7.30	9.21	2.93	3.89	2.84	1.53	2.28	1.70	1.02	2.01	1.42	1.35	1.92	1.34	1.08	1.68	1.18	1.23	1.65	1.16	

\* Moisture contents: Norfolk sand 3.83 per cent, Sassafras sandy loam 9.83 per cent, Hartsells silt loam 16.42 per cent, Cecil clay 19.73 per cent, Hagerstown clay 20.78 per cent, Hagerstown silty clay loam 23.70 per cent, and Chester clay loam 24.38 per cent.

nents and the added materials that tend to reduce the osmotic pressure increase in the soil solution below that obtained in the absence of soil.

#### CHOICE OF BASIS FOR THE SALT INDEX

It is apparent that the salt index could have been defined in terms of the osmotic effects in water solution in the absence of soil. It remains therefore to inquire whether such an index gives more helpful data by which to judge the probable burning effects of fertilizers than does the salt index described above. For materials that give about the same osmotic pressure in water solution as in the soil solution, no serious differences in the two index values should result. Such materials, however, are exceptional, aside from sodium nitrate itself, which was chosen as the reference material for the salt index largely because of that property. The two indexes would be enormously different for the phosphates, and since most fertilizers contain relatively large quantities of phosphates, it is apparent that indexes based on values determined in water solutions would be highly misleading, indicating a higher burning effect than is actually experienced because of the high fixing power of most soils for phosphates. It has also been suggested that the soluble salt content of a fertilizer be used as an index to the tendency of the fertilizer to injure crops. The salt indexes based on soil solution and on water solution and the total soluble salts of nine mixed fertilizers are compared in the following tabulation:

FERTILIZER NUMBER	SALT INDEX		TOTAL WATER-SOLUBLE SALTS
	Determined on Norfolk	Water basis	
			<i>per cent</i>
101	24.7	34.1	41.2
102	41.9	47.7	64.0
103	38.9	43.6	51.4
104	55.6	62.7	77.4
105	22.6	34.4	35.5
106	64.2	69.4	67.4
107	21.2	35.9	39.7
108	63.3	74.8	73.8
109	61.9	74.4	73.8

The salt index, water basis, does not reproduce the index as actually determined on the Norfolk soil. Differences as great as 33 per cent occur in this soil, which should have a minimum of soil effects due to its very low colloid content. The total water-soluble salts would not be expected to agree numerically but would serve the same purpose if they bore a constant ratio to the indexes determined on soil. This ratio, however, varies from 0.6 to nearly 1.0, and a scale based on water-soluble salt in the fertilizer presents quite a different picture from the proposed salt-index scale. Neither the water-basis indexes nor the soluble salt contents place the fertilizers used here in the same order, with respect to their tendency to injure crops, as they are placed by the determined salt index. It has already been pointed out that, in the presence of soil, the

phosphates fail to give more than a small fraction of the osmotic pressure that they give in water solution only. This is one of the reasons why the water-basis index and the total soluble salts do not give satisfactory scales by which to gauge crop-injuring tendencies. It should also be mentioned in this connection that the calcium sulfate present in a fertilizer may be nearly all included in the salts dissolved in the determination of water-soluble salt, whereas only a small portion of it may be dissolved in the soil solution. It may be said therefore that neither of the water-solution indexes is as good a measure of the tendency to injure crops as is the proposed salt index.

#### SUMMARY

A study has been made of the effect of fertilizer materials and mixed fertilizers on the concentration of the soil solutions of several soils. The solutions were obtained from soils containing water corresponding to 75 per cent of the moisture equivalent, and their concentrations were expressed in terms of osmotic pressure. The widely varying osmotic effects of individual materials on the soil solution and the lack of correlation between these effects and those found in water solutions in the absence of soil have been pointed out. This is especially noticeable with the phosphate salts.

A new quantity, the salt index of fertilizers, is proposed as a means of expressing differences in the probable effects of different fertilizers or fertilizer constituents upon the soil solution and consequently upon the tendency of the fertilizer to injure crops by undue osmotic pressure in the soil solution. This index can be calculated for any mixed fertilizer of known composition.

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# A NOTE ON ELECTRICAL METHODS OF DETERMINING SOIL MOISTURE

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The routine sampling and treatment of soil for moisture content determination is time-consuming, and in some cases may not even be permissible. It is therefore natural that much attention should have been paid to alternative indirect methods, of which those depending on the electrical properties of soil seem to have attracted the greatest attention (1, 4, 6). The purpose of this brief note is to draw attention to some dangers inherent in the method. A very full list of references to work on the subject up to 1934 has been given by Smith-Rose (9).

A system of electrodes embedded in a medium other than a perfect insulator with a dielectric constant of unity seems to be regarded commonly as a single condenser with a uniform dielectric. In practice it is almost impossible to provide such a condition, for the electrodes are generally to be considered as being surrounded by sheaths separating them from the main dielectric (7).

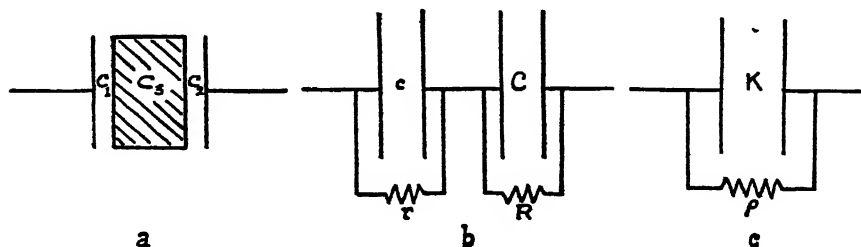


FIG. 1

The effects of such sheaths were impressed very firmly on the writer's mind some years ago during work on the dielectric constant of ionized air (2). Whether the sheath is due to the exclusion of ions (2, 10) or to imperfect mechanical contact, the effect is the same; the condenser must be regarded as a combination of condensers in series, the dielectrics of the component condensers having different properties. The result, described by Hartshorn in connection with tests of good dielectrics (7), is profoundly to affect the resistance and capacitance of the condenser, particularly when the dielectric is very leaky, as is the case with moist soil or plaster of paris condensers.

In figure 1-a the sheaths are shown much magnified for clarity and may be regarded as condensers  $C_1$  and  $C_2$  in series with the condenser  $C_s$ , the dielectric of which is the moist porous medium. The system may be represented diagrammatically as in figure 1-b, in which the moist dielectric corresponds to a condenser of capacitance  $c$  and shunt resistance  $r$  while the sheaths, taken together, are represented by the condenser of capacitance  $C$  and shunt resistance  $R$ . The



impedances are  $z$  and  $Z$  respectively. This combination is electrically equivalent to the single condenser of capacitance  $K$  and shunt resistance  $\rho$  (impedance  $Z$ ) of figure 1-c, and it is these latter values which are measured by the usual bridge methods. We must therefore examine the dependence of these values on those in which we are interested, namely,  $c$  and  $r$ . The simplest way to derive the required relationship is to use the method of complex quantities. Writing  $j = \sqrt{-1}$ , and  $\omega = 2\pi n$ , (where  $n$  is the frequency of alternation of the current), we have

$$1/z = 1/r + j\omega c$$

whence

$$z = r(1 - j\omega cr) / (1 + \omega^2 c^2 r^2)$$

Similarly

$$Z = R(1 - j\omega CR) / (1 + \omega^2 C^2 R^2)$$

$$Z = \rho(1 - j\omega K\rho) / (1 + \omega^2 K^2 \rho^2)$$

Also

$$Z = z + Z$$

Equating real and imaginary parts, we have

$$r/(1 + \omega^2 c^2 r^2) + R/(1 + \omega^2 C^2 R^2) = \rho/(1 + \omega^2 K^2 \rho^2) \quad (1)$$

$$cr^2/(1 + \omega^2 c^2 r^2) + CR^2/(1 + \omega^2 C^2 R^2) = K\rho^2/(1 + \omega^2 K^2 \rho^2) \quad (2)$$

When  $\omega$  is very large, equation (2) reduces to

$$1/c + 1/C = 1/K$$

which is the ordinary expression for condensers in series. Furthermore, since the sheath thickness in the soil condenser is very small,  $C$  is much larger than  $c$ , and the equation further simplifies to

$$c = K$$

In the same circumstances, (1) reduces to

$$r = \rho$$

so that the measured values of capacitance and resistance are the true soil values. For this approximation to be valid,  $\omega^2 c^2 r^2$  must be large compared with unity; for a soil condenser of normal size,  $c$  may be of the order of 100 pF<sup>1</sup>, calculated on a basis of a dielectric constant of 80 at saturation, while  $r$  may be of the order of 100 ohms, so that  $\omega$  must be much larger than  $10^8$ , i.e., the current frequency must considerably exceed 10 megacycles per second. The highest frequency used in soil work, to the writer's knowledge, is 37.5 megacycles (5), 4 megacycles not often being exceeded (6, 8, 9). Usually the frequency lies within the audible range, when  $\omega^2 c^2 r^2$  may be neglected in comparison with unity. Equations

<sup>1</sup> The convenient small unit of capacitance, the picofarad, was introduced by A. Campbell in 1922, to replace the more cumbrous nomenclature, the micromicrofarad. It is unfortunate that some confusion may be caused by the recent use of pF, the abbreviation of this unit, to indicate the logarithm of suction pressure, a quantity that has no place in fundamental soil-water relationships.

(1) and (2) may be further simplified, for the sheaths may be assumed to be perfectly insulating, so that we may write  $R = \infty$ . We then get

$$\rho/(1 + \omega^2 K^2 \rho^2) = r \quad (3)$$

$$K\rho^2/(1 + \omega^2 K^2 \rho^2) = cr^2 + 1/\omega^2 C \quad (4)$$

The magnitude of the sheath effects may be examined by considering one or two hypothetical cases.

First, let us suppose that the true capacitance of the soil or plaster condenser is 100 pF, a reasonable value, the true resistance is 1,000 ohms and  $\omega = 10,000$ .

TABLE 1

*Influence of sheath formation on apparent capacitance and resistance of soil condenser*

When  $\omega = 10,000$ ;  $c = 10^{-10}$  farads;  $r = 1,000$  ohms

$C$	$\rho$	$K$
<i>farads</i>	<i>ohms</i>	<i>farads</i>
$\infty$	1,000	$10^{-10}$
$10^{-3}$	1,000	$1.1 \times 10^{-10}$
$10^{-4}$	1,000	$2.0 \times 10^{-10}$
$10^{-5}$	1,001	$1.1 \times 10^{-9}$
$10^{-6}$	1,010	$10^{-8}$
$10^{-7}$	2,000	$5.0 \times 10^{-8}$
$10^{-8}$	$10^6$	$10^{-8}$
$10^{-9}$	$10^7$	$10^{-9}$

TABLE 2

*Influence of resistance of dielectric on apparent capacitance and resistance of soil condenser*

When  $\omega = 10,000$ ;  $c = 10^{-10}$  farads;  $C = 10^{-6}$  farads

$r$	$\rho$	$K$
<i>ohms</i>	<i>ohms</i>	<i>farads</i>
$10^6$	$2.0 \times 10^6$	$0.5 \times 10^{-10}$
$10^5$	$1.01 \times 10^5$	$10^{-10}$
$10^4$	$10^4$	$2.0 \times 10^{-10}$
$10^3$	$10^3$	$10^{-8}$
$10^2$	$10^2$	$10^{-6}$
10	10	$10^{-4}$

We may now give  $C$  a succession of values varying from  $\infty$ , corresponding to perfect contact between the electrodes and the dielectric medium, to small values corresponding to very imperfect contact. The results are shown in table 1, obtained by substituting the known values in (3) and (4) and solving for  $K$  and  $\rho$ . Thus we see that imperfect contact, or any other cause of sheath formation, can increase the apparent capacitance in this case by more than a hundredfold. The apparent resistance is less sensitive to sheath influence; in table 1 it is increased by only 10 per cent when the capacitance is increased by a factor of 100.

As a final example, we may calculate the variation of  $K$  and  $\rho$  when  $r$  alone varies. The results are given, for reasonable values of  $\omega$ ,  $c$ , and  $C$ , in table 2. This case is of the greatest importance to those measuring moisture content by this method. We thus see that a reduction of resistance of the dielectric is itself responsible for an apparent large increase of capacitance, quite irrespective of any increase of dielectric constant.

A rough test of these conclusions was made by measuring the resistance and capacitance between two parallel plate electrodes immersed first in distilled water, then in tap water, and finally in a very weak solution of  $\text{NaHCO}_3$ . Dissolved salts are known to have very little effect on the dielectric constant of water, whereas the conductivity is, of course, determined almost solely by the concentration of solute. The measured cell resistances were 30,510 ohms, 494 ohms, and 127 ohms respectively, the capacitance changing from 60 pF to  $0.01\mu\text{F}$ . and then to  $0.1\mu\text{F}$ .

The results of Anderson and Edlefsen (1) also lend support to these views. The plaster block cell which they used has a capacitance, calculated from its dimensions, which cannot exceed about 50 pF, yet the measured capacitance at maximum moisture content is said to be  $0.07\mu\text{F}$ . Furthermore, the range of variation with moisture content, expressed as the ratio of maximum to minimum capacitance, exceeds the dielectric constant of water!

Since the variations of capacitance of a soil condenser with moisture content seems to be really but an indirect consequence of variation of resistance and is greatly dependent on contact conditions which are largely out of the control of the experimenter, it would seem preferable to measure the resistance directly, particularly since we have seen that this is relatively insensitive to sheath formation. If there should be any advantage in measuring capacitance, there would appear to be possibilities in the application of the alternating current potentiometer (3) in conjunction with four-electrode cells, since no current is taken from the potential electrodes at the balance point and therefore sheath formation is quite without effect. The apparatus is, however, bulky, and it would not be an easy matter to design it as a portable field set. The alternative is to work at very high frequencies.

#### SUMMARY

The unreliability of measurements of capacitance of soil condensers as an indication of moisture content is stressed and is explained by demonstrating the profound effects of poor electrode contact when the dielectric is very leaky.

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# FREEZING POINTS OF A GROUP OF CALIFORNIA SOILS AND THEIR EXTRACTED CLAYS<sup>1</sup>

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The flow of soil moisture and its utilization by plants depend in part upon the force with which water is held by the soil, and calculations of the free energy of soil moisture provide a rational approach to the consideration of such phenomena. The present work was undertaken in order to investigate by means of the cryoscopic, or freezing-point method, the magnitudes of the free energy of soil water at different water contents and also some of the factors affecting these magnitudes.

Schofield and Botelho da Costa (20) were the first to use the cryoscopic method for determining the difference between the free energy of water in bulk and that of water in moist soil. Bodman and Day (1) improved the technique by the substitution of a sensitive thermocouple for the Beckmann thermometer and by better isolation of the sample from the freezing bath. Further improvements of technique have been made and are discussed hereinafter.

Schofield (21) used the following equation in his calculation, by the freezing method, of the difference in free energy:

$$H = \frac{L_f}{T \cdot g} \cdot t \quad (1)$$

in which the symbols were defined as,

$H$  = height of liquid column to give equivalent suction (cm.)

$L_f$  = latent heat of fusion of water ( $3.336 \times 10^9$  ergs·gm.<sup>-1</sup>)

$t$  = freezing point depression of water in soil (°C.)

$T$  = freezing point of pure water (= 273.18° absolute)

$g$  = acceleration of gravity (= 981 cm.-sec.<sup>-2</sup>)

The context of Schofield's paper seems to make it evident that by "height of liquid column to give equivalent suction" is meant the height,  $H$ , of a column of water which the water in the moist soil could support when connected to a water reservoir, through a suitable apparatus including a water column of adjustable height, the entire system being held at 1 atmosphere of pressure and 273.18° absolute. The tensiometer is such an instrument. But it must be made clear that when measured by means of a tensiometer,  $H$  can only be defined as equivalent to the free energy difference for those special cases in which the soils contain no dissolved salts. This limitation was recognized by Schofield in a later paper (22).

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An equation has been developed by Day (5), who used the term "moisture potential,"  $\mu$ , to define the free energy of escape of soil water, when consideration is given to the influence of pressure, temperature, and solutes. In the present paper the same meaning is retained for the moisture potential, viz.

$$\mu = \frac{L_f \cdot T}{T_0} \quad (2)$$

in which

$L_f$  = latent heat of fusion of water ( $= -3.336 \times 10^9$  ergs·gm.<sup>-1</sup>)

$T$  = freezing point depression of water in soil (°C.)

$T_0$  = freezing point of pure water (273.18° absolute)

and the moisture potential is obtained in ergs per gram of water. For the special case of solute-free soils, equation (2) may be written in the form of equation (1).

Schofield also introduced the term "pF," which has now come into rather extensive use, and which represents the common logarithm of  $H$  [equation (1)]. It must again be pointed out that when a tensiometer is used, the term "pF" expresses the logarithm of the free energy of the soil moisture only in the absence of solutes. The term "pF" has the distinct value of abbreviating large numbers, but in order that ambiguity may be avoided in the discussion of the potential measurements, it has not been used in the present paper.

#### APPARATUS

##### *Description*

The equipment is a refinement of that used earlier (1), although no change has been made in the essential features. The soil sample, weighing approximately 5 gm., was enclosed in a small Dewar flask equipped with a thermojunction, and the assembly was immersed in a kerosene bath at a suitable temperature. The reference temperature was produced and maintained by means of a second Dewar flask, filled with a mixture of ice and water and containing the other junction of the thermocouple. The e.m.f. produced by the thermocouple was measured by a sensitive galvanometer and potentiometer, and the difference in temperature between the two junctions was computed from calibration tables.

The Dewar flasks used as freezing jackets were made of two concentric pyrex test tubes (fig. 1) which had been sealed together at the top, attached overnight to a Hyvac pump until the pressure within the jacket was reduced to that equivalent to about  $10^{-5}$  mm. mercury, and then sealed at the bottom. The thermojunction (fig. 1) was constructed of B. & S. 36-gauge copper and B. & S. 30-gauge constantan wire. These were twisted together and soldered into a small brass tip weighing 2 gm., constructed in such a way that the end bearing the wires could be slipped snugly into a pyrex glass lead-tube and cemented in place. About half of the brass tip was left protruding. The glass lead-tube passed through a rubber stopper which served to close the freezing jacket after sample and thermojunction had been inserted.

The cold bath in which the freezing jackets were immersed consisted of a 2-

gallon glass aquarium jar filled with kerosene and fitted with a transite cover. This vessel was immersed in a larger metal tank of kerosene maintained at approximately  $-5^{\circ}\text{C}.$  by means of a  $\frac{1}{4}$  h.p. Frigidaire unit. The inner bath could be regulated to any temperature between  $0^{\circ}$  and  $-5^{\circ}\text{C}.$  and controlled within  $\pm 0.1^{\circ}$  of the desired temperature by means of a mercury thermoregulator, an electric heater, and a motor-driven stirrer. Holes bored in the transite cover permitted insertion of the freezing jackets, for which suitable clamps were provided. Four such jackets with thermocouples could be accommodated at one time.

The equipment for measurement of the thermal e.m.f. consisted of a Leeds and Northrup type HS galvanometer having a measured sensitivity of 0.0860 microvolt per millimeter with the scale at 1 meter, and a type K-2 potentiometer, the

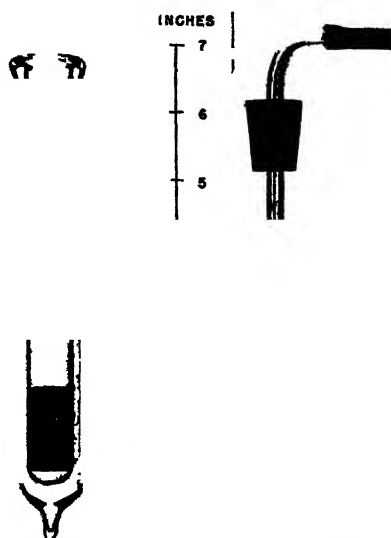


FIG. 1. LEFT, DEWAR FLASK FREEZING JACKET CONTAINING 5-GM. SOIL SAMPLE; RIGHT, BRASS-TIPPED COPPER-CONSTANTAN THERMOCOUPLE

least reading for the revolving head slidewire of which corresponded to an e.m.f. of 0.5 microvolt.

### *Calibration*

The thermocouples were calibrated through the use of an empirical relationship between e.m.f. and temperature for copper-constantan couples given by Bridgman (3). A preliminary measurement with  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , held at its transition temperature, showed close agreement with the empirical equation. In order to check the thermocouples in the range in which they were to be used, it seemed desirable to determine the freezing point depressions of known osmotic solutions for which accurate data were available elsewhere. For this purpose, aqueous sucrose solutions of various concentrations up to 1.07 molal were employed. The data are given in table 1 and compared with data interpolated from Landolt-



Börnstein tables (10) by means of the least-squares equation:  $\Delta T = 1.8131 m + 0.2318 m^2$ , where  $m$  is molality, i.e., the moles of sucrose per 1000 gm. of water, and  $\Delta T$  is the interpolated value of the freezing point depression. The agreement was considered to be sufficiently good to justify the use of the Bridgman relationship for the freezing determinations of soils to be reported.

TABLE 1  
*Observed and calculated freezing point depressions of aqueous solutions of sucrose*

MOLS OF SUCROSE IN 1000 GM. OF WATER (MOLALITY)	FREEZING POINT DEPRESSIONS	
	Observed	Calculated from Landolt-Börnstein
	°C.	°C.
0.0000	-0.016	0.000
0.0000	0.008	0.000
0.0000	0.005	0.000
0.0000	-0.011	0.000
0.0153	0.037	0.028
0.0163	0.040	0.030
0.0147	0.037	0.027
0.0164	0.045	0.030
0.0404	0.091	0.073
0.0408	0.085	0.073
0.0410	0.083	0.074
0.0386	0.083	0.070
0.0842	0.170	0.155
0.0857	0.181	0.157
0.0848	0.181	0.156
0.0863	0.162	0.158
0.2150	0.448	0.401
0.2176	0.453	0.406
0.2173	0.453	0.407
0.2161	0.458	0.403
1.0604	2.233	2.183
1.0578	2.257	2.177
1.0602	2.228	2.183
1.0680	2.230	2.201

All directly observed values of the freezing points of soils and solutions are reported to 0.001°C.<sup>3</sup> In those cases in which it was necessary to interpolate from the experimental curves, however, it was usually possible to obtain the desired reading to no more than  $\pm 0.01^\circ\text{C}$ . (see, for example, table 3). An exception occurs in the data of Landolt-Börnstein, which were numerous and, as has been mentioned, readily permitted the formulation of a least-squares equation from which interpolations were obtained to 0.001° (see right-hand column of table 1).

<sup>3</sup> The entire instrumental assembly had a sensitiveness of  $\pm 0.001^\circ\text{C}$ .

## EXPERIMENTAL PROCEDURE

*Soil types used*

Fourteen different surface soils were used, all of which are important agricultural types in California. No saline soils were included. The soil series have been described by Shaw (23) and their properties summarized by Storie and Weir

TABLE 2

*Geologic origin of soils used and climatic characteristics\* of sample areas (26, 30, 31)*

SOIL		PARENT MATERIAL	NORMAL ANNUAL PRECIPITATION	NORMAL ANNUAL MEAN TEM- PERATURE	P-E INDEX	CLIMATIC TYPE†
Number	Type					
			<i>inches</i>	<i>°F.</i>		
S48	Hanford loamy sand	Granitic rock, alluvium	16.06	59.4	33	Dry subhumid
1250	Oakley sand	Dune sands of mixed origin	12.02	62.1	24	Semiarid
626	Holland sandy loam	Granitic rock, residuum	22.37	61.4	47	Dry subhumid
623	Sierra sandy loam	Granitic rock, residuum	22.37	61.4	47	Dry subhumid
1251	Yolo fine sandy loam	Mixed sedimentary rock, alluvium	16.14	61.6	32	Dry subhumid
607	Antioch loam	Mixed sedimentary rock, alluvium	12.02	62.1	24	Semiarid
1252	Yolo clay loam	Mixed sedimentary rock, alluvium	16.14	61.6	32	Dry subhumid
1253	Yolo clay (i)	Mixed sedimentary rock, alluvium	16.14	61.6	32	Dry subhumid
616	Vina loam	Basic igneous rock, alluvium	24.04	62.5	51	Moist subhumid
1254	Yolo clay (ii)	Mixed sedimentary rock, alluvium	16.14	61.6	32	Dry subhumid
611	Yolo silt loam	Mixed sedimentary rock, alluvium	16.14	61.6	32	Dry subhumid
619A	Aiken clay loam	Basic igneous rock, residuum	59.34	55.1	165	Superhumid
604A	Altamont clay	Mixed sedimentary rock, residuum	13.70	59.4	27	Semiarid
613	Stockton clay	Mixed sedimentary rock, residuum	16.55	62.3	34	Dry subhumid

\* Precipitation and temperature data refer to nearest Weather Bureau Station (32).

† All soils developed under summer rainfall deficiency.

(26). The soils, together with an expression of the climates of the sample areas, are listed in table 2. In all cases the name assigned to the soil sample in the table and used throughout the paper is the type name given by the soil surveyors in the field. The type name should not, therefore, be taken as indicative of an exact range in particle size proportions. The content of clay in these samples finer

than  $2\ \mu$  effective diameter is included in table 3. Three of the soil types (Aiken clay loam, Stockton adobe clay, and Yolo silt loam) have also been used by Botelho da Costa (2), although the samples used in the investigation here reported are not the same samples as were used by that author and were collected independently.

### *Preparation of samples*

In order to obtain uniform distribution of moisture within the samples, water was added from a burette at a uniform rate through an atomizer nozzle, which produced a fine spray at a known rate of delivery. Successive thin layers of soil held in a 4-ounce wide-mouthed bottle were sprayed with known volumes of

TABLE 3

*Freezing point depression, moisture potential, and pressure potential at the moisture equivalent*

SOIL NUMBER	CONTENT OF CLAY < $2\mu$	MOISTURE EQUIVALENT	FREEZING POINT DEPRESSION	MOISTURE POTENTIAL	PRESSURE POTENTIAL*
	<i>per cent</i>	<i>per cent</i>	$^{\circ}\text{C.}$	$\text{ergs/gm.} \times 10^{-6}$	$\text{ergs/gm.} \times 10^{-6}$
S48	4.1	5.5	0.11	-1.3	.
1250	4.6	4.3	0.19	-2.3	-0.25
626	8.0	11.5	0.02	-0.24	....
623	11.7	16.1	0.06	-0.73	...
1251	12.8	18.1	0.10	-1.2	-0.12
607	16.0	16.2	0.06	-0.73	....
1252	17.2	22.5	0.08	-0.98	-0.20†
1253	23.2	25.0	0.10	-1.2	-0.14
616	26.5	26.9	0.10	-1.2	....
1254	33.1	26.3	0.10	-1.2	-0.27†
611	34.7	36.0	0.08	-0.98	....
619A	41.8	31.2	0.07	-0.85	....
604A	46.3	27.7	0.10	-1.2	....
613	62.7	39.6	0.13	-1.6	....

\* From drying curves obtained from tensiometer measurements by Moore (13).

† Extrapolated.

water until 20 gm. of soil had been moistened to the desired degree. After addition of water, the bottle was closed with a rubber stopper and stored in the dark for a week before use. A 5-gm. sample of soil was then carefully removed from the bottle, gently molded into cylindrical shape, and placed in the jacket for measurement of the freezing point.

### *Technique of making freezing measurements*

In preliminary studies it was found desirable, before inception of freezing, to bring the sample to thermal equilibrium with the bath, the temperature of which should not be more than two degrees below the freezing point of the sample (1). The bath temperature was therefore set to the appropriate value, and the jacket containing the sample was inserted. Approximately two hours were then required for attainment of equilibrium with the bath. After the initial temperature was recorded, freezing was induced by tapping the thermocouple tube, and

the e.m.f. was measured as a function of time after freezing began. A maximum temperature was usually reached within two to four minutes after freezing was induced. The ensuing rate of drop was very slight in all cases, and for this reason the maximum has been chosen as the "freezing point." The data from these temperature-time curves were preserved in order to make the appropriate moisture content corrections. At the completion of the run the sample was removed from the jacket and placed in a glass weighing bottle for determination of moisture loss at 105°C.

### *Moisture content correction*

The formation of ice during the freezing process reduces the amount of liquid water in the soil and therefore when the freezing temperature is reached an appreciable amount of water has already been changed from liquid to solid state. For this reason Schofield and Botelho da Costa (20) considered that the "effective moisture content," obtained by subtracting from the total water content the amount of ice present, is the liquid water which properly corresponds to the observed freezing point. Because of uncertainty concerning the uniformity of the distribution of the water in the soil, limitations in the validity of this procedure are recognized; nevertheless, the same assumption will be made in the present investigation.

If the amount of heat liberated during the freezing process is known, the amount of ice may be calculated from the changes in heat capacity both of the individual constituents of the system and of the system as a whole. The "system" is considered to include the moist soil sample and the part of the jacket and of the thermocouple in direct contact with the sample. The change in heat capacity of the individual constituents of the system was calculated from their respective heat capacities and the difference between initial temperature and freezing point. The change in heat capacity of the system as a whole over the same time interval was determined by means of a principle of calorimetry according to which the rate of exchange of heat between external bath and calorimetric chamber is proportional to the thermal head (35); the proportionality constant, termed the "thermal leakage modulus," was found to be 0.20 calorie per minute per degree, for the jackets used. The change in heat capacity was calculated by multiplying the thermal leakage modulus by the area enclosed by the curve of temperature versus time. The total heat evolved during the formation of  $m$  grams of ice was computed by adding up all changes in heat content of the system between initial and final states, and  $m$  was obtained by dividing the total heat evolved by the heat of fusion ( $333.6 \times 10^7$  ergs per gram). The effective moisture content,  $P$ , is given by

$$= 100 \left( \frac{M - m}{w} \right)$$

in which  $M$  is the mass of liquid water plus ice and  $w$  is the weight of the sample after drying in the oven at 105°C. In the measurements reported in this paper the moisture percentage corrections varied from approximately 0.5 to 2 per cent for soils, up to nearly 5 per cent for soil clays.

## FREEZING POINTS OF SOILS IN RELATION TO WATER CONTENT

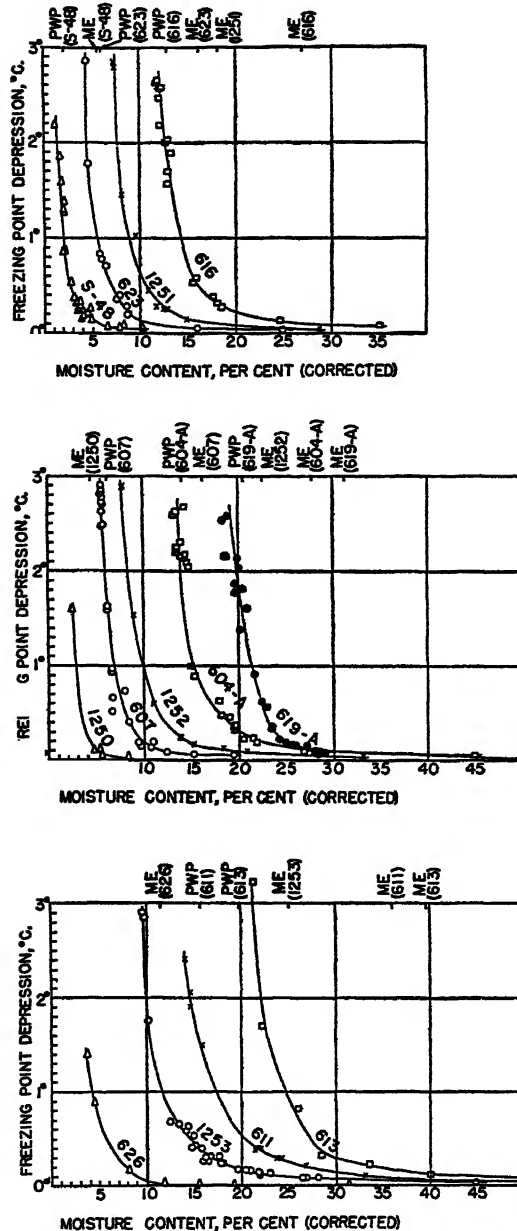
Altogether 225 freezing measurements were made of the 14 soils at many different moisture percentages. The results are shown in figure 2, in which the grouping adopted is only for the purpose of avoiding confusion caused by overlapping curves. The scattering of the experimental points about the free-hand curves indicates the reproducibility of the freezing determinations. The corresponding moisture equivalents of the soils are also shown on the graphs.

*Moisture potential at the moisture equivalent*

The freezing point depressions at the moisture equivalent were obtained graphically from the curves. The corresponding moisture potentials were calculated by means of equation (2). These data are entered in table 3. The extreme range in moisture potentials is from  $-0.24 \times 10^6$  for Holland sandy loam, to  $-2.3 \times 10^6$  for Oakley sand, but the values for 12 of the soils lie within the much narrower range  $-0.73 \times 10^6$  to  $-1.6 \times 10^6$  ergs per gram. The mean value for all is  $-1.12 \times 10^6$  ergs per gram.

According to Moore, who used the porous cup tensiometer method, the pressure potentials of soils at their moisture equivalents are of the order of  $-0.15 \times 10^6$  ergs per gram, equivalent to a tension of about 150 cm. of water. Russell and Richards (19) however, obtained higher values by means of the special centrifugal method which they developed. Five of the soils that were used in the freezing measurements had been used by Moore in an earlier experiment (13). In column 6 of table 3 are given values of the pressure potentials of these soils at their moisture equivalents which were obtained from Moore's curves. It became apparent from these comparisons that an important factor, not measured by the tensiometer, was operating to depress the moisture potentials as calculated from the freezing points. The electrical conductivities accordingly were measured on 1:1 aqueous suspensions of all the soils used in this investigation in order to estimate the abundance of dissolved solutes. The conductivity cell consisted of plane, parallel, platinum electrodes. The cell was calibrated with 0.01 N KCl, and the cell factor was found to be 4.45 cm. The aqueous suspensions were prepared by adding to a 20-gm. sample of air-dry soil a weight of boiled, distilled water equivalent to the weight of oven-dry soil present. The shaker bottles in which they had been placed were stoppered, allowed to stand for 8 hours, and then shaken for 1 hour in a reciprocating shaker. The bottles were placed in an upright position and the suspensions allowed to settle. The supernatant liquid was then poured into the electrode vessel and the net resistance in ohms determined by means of a Wheatstone bridge operating on 1000 cycles A.C. Multiplication by the cell factor gave the specific resistance in ohm-centimeters.

The method of Sokoloff (25) was employed in estimating the concentration of electrolytes in the liquid, the assumption being made in the calculation that the concentrations of sodium and chloride ions, respectively, were less than 20 m.e. per liter. The electrolyte concentration at the moisture equivalent was then estimated by assuming that the quantity and quality of dissolved solutes under-



went no change during reduction in moisture content from a 1:1 ratio down to the moisture equivalent, and that the concentration of solutes, and also the osmotic potential, are inversely proportional to the moisture content.

The osmotic potential,  $\omega$ , was determined from the calculated electrolyte content at the moisture equivalent by means of Day's (5) equation

$$\omega = -\frac{RT}{1000} \cdot m_i \quad (3)$$

in which

$R$  = gas constant (ergs·mols<sup>-1</sup>·degrees absolute<sup>-1</sup>)

$T$  = temperature (degrees absolute)

$m_i$  = sum of molalities of all solutes present

The conductivities were measured at 24°C. In the calculations the low solute concentrations which were obtained as milligram equivalents per liter were considered equal to molality  $\times 1000$ . Since, according to Guggenheim (7, p. 104)

TABLE 4

*Comparison of osmotic potential and moisture potential at the moisture equivalent*

SOIL NUMBER	SPECIFIC CONDUCTANCE OF 1:1 SUSPENSION	ELECTROLYTE CONCENTRATION OF 1:1 SUSPENSION	ELECTROLYTE CONCENTRATION AT MOISTURE EQUIVALENT	OSMOTIC POTENTIAL AT MOISTURE EQUIVALENT ( $\omega$ )	MOISTURE POTENTIAL AT MOISTURE EQUIVALENT ( $\mu$ )
	<i>mhos/cm. <math>\times 10^4</math></i>	<i>m.e./liter</i>	<i>m.e./liter</i>	<i>ergs/gm. <math>\times 10^{-8}</math></i>	<i>ergs/gm. <math>\times 10^{-8}</math></i>
S48	20.3	4.68	85.1	-2.1	-1.3
1250	12.5	2.88	67.0	-1.7	-2.3
623	10.5	2.42	15.0	-0.4	-0.73
1251	28.1	6.70	37.0	-0.9	-1.2
607	18.7	4.30	26.5	-0.7	-0.73
1252	30.4	7.00	31.1	-0.8	-0.98
1253	34.0	7.82	31.3	-0.8	-1.2
616	54.9	12.62	46.9	-1.1	-1.2
1254	28.1	6.46	24.6	-0.6	-1.2
611	68.0	15.64	43.5	-1.1	-0.98
619A	11.3	2.60	8.3	-0.2	-0.85
604A	46.7	10.76	48.8	-1.2	-1.2
613	....	....	....	....	-1.6
Mean .....				-0.97	-1.19

for solutions less than one-tenth molal, the temperature is without effect upon the ionic activity, the osmotic potentials calculated at 297° absolute may be directly compared with the moisture potentials calculated at 273° absolute, from the freezing points. The results of these calculations are given in table 4.

Most of the osmotic potential values are numerically lower than those for the moisture potential. Excluding soils S48 and 611, for which the calculated osmotic potential exceeds the moisture potential, the average ratio  $\omega:\mu$  is 0.7. The conclusion to be drawn is that for these soils the data are consistent with the hypothesis that at the moisture equivalent the depression of the moisture potential is largely due to solutes present in the soil moisture. Different soils which differ in their solute concentration at the moisture equivalent must, therefore,

be expected to differ considerably in their moisture potential at that moisture content.

These conclusions are in agreement with the results of freezing measurements obtained by Burd and Martin (4) for another group of California soils. They showed clearly that at high moisture contents the freezing point depression of the soil was always slightly in excess of, but agreed rather closely with, that of the displaced solution. The freezing point depressions which Burd and Martin obtained for moist soils are of the same order of magnitude as those reported in the present paper at moisture contents about the moisture equivalent, thus suggesting similar solute concentrations for the two lots of soils. Numerous investigators (2, 8, 17) have shown that leaching diminishes the freezing point depression of soils at high moisture contents, and this has been attributed chiefly to the removal of electrolytes.

Aside from the small contribution of the pressure potential, the observed variations in moisture potential at the moisture equivalent are largely due to variations in solute concentrations. The results show that the activity of the soil moisture may be depressed or increased, respectively, by the addition or removal of solutes.

#### *Moisture potential at the permanent wilting percentage*

During the course of the investigation, and after most of the freezing point measurements had been completed, the stock supply of soils 1250 to 1254, inclusive, was destroyed by fire in 1938. On this account the measurements of the permanent wilting percentages could not be obtained for all the soils. For those soils whose wilting point was measured, sunflower seeds were planted in cans containing 400 gm. of soil, which was immediately brought to field capacity. After one or two additional irrigations the plants had developed three sets of leaves and were then allowed to wilt. When the top leaves were definitely wilted and the lower sets beginning to droop, the plants were placed in a humid chamber. If they failed to recover within several hours they were removed and each can, with contents, was weighed. A correction was applied for the moisture content of the plant roots by assuming their moist weight equalled half that of the tops, and that eight tenths of this weight was water. The results are included in table 5. Statistical examination showed that the distribution of values within a set of replicates for a single soil was in good agreement with data by Veihmeyer and Hendrickson (33) and with unpublished data by Veihmeyer.

The freezing point depressions corresponding to the permanent wilting percentage have been obtained from the curves of figure 2. The corresponding moisture potentials have been calculated by means of equation (2) and are shown in table 5. The mean value of  $-18.1 \times 10^6$  ergs per gram corresponds to a pressure of about 18 atmospheres. Table 6 summarizes the moisture potential values obtained by others for the permanent wilting percentages of different soils, using different methods. Recent measurements of Richards (18) by the pressure membrane method indicate values of the same order of magnitude, although the actual values at the wilting point were not reported.



Considerable differences exist in the moisture potentials of these soils (table 5) at their respective wilting points. Veihmeyer and Hendrickson (34) using the seed-absorption method of Shull (24) with other soils, and Schofield and Botelho da Costa (20) using the freezing point method, also obtained differences in this

TABLE 5

*Freezing point depression and moisture potential at the permanent wilting percentage*

SOIL NUMBER	PERMANENT WILTING PERCENTAGE	MOISTURE EQUIVALENT PERMANENT WILTING PERCENTAGE	FREEZING POINT DEPRESSION AT PERMANENT WILTING PERCENTAGE	MOISTURE POTENTIAL AT PERMANENT WILTING PERCENTAGE
			°C.	$\text{ergs/gm.} \times 10^{-8}$
S48	2.0	2.74	1.16	-14.2
623	5.9	2.75	0.84	-10.3
607	6.1	2.67	1.80	-22.0
616	12.8	2.10	1.85	-22.6
611	15.7	2.30	1.46	-17.8
619A	20.5	1.52	1.48	-18.1
604A	14.0	1.98	1.80	-22.0
613	19.8*	2.00	....†	....†
Mean.....			1.48	-18.1

\* Wilting determination by T. J. Marshall.

† Freezing point could not be obtained at the permanent wilting percentage.

TABLE 6

*Moisture potentials at the permanent wilting percentage as obtained by different investigators*

SOIL	PERMANENT WILTING PERCENTAGE	MOISTURE POTENTIAL	INVESTIGATOR AND METHOD USED
		$\text{ergs/gm.} \times 10^{-8}$	
Sand.....	1.39	-11.6	Thomas (28), vapor pressure
Greenville loam.....	9.30	-17.5	
West Logan clay loam.....	11.00	-11.6	
Average of three soils.....	....	-18.0	Edlefsen (6), vapor pressure
M.....	3.7	-11.5	Veihmeyer and Hendrickson (34), water ad- sorption by seeds
DS.....	4.2	-22.7	
Y.....	8.9	0	
MG.....	10.2	-21.6	
O.....	12.5	-25.4	
YC.....	14.0	-13.7	

respect, although the logarithmic character of the pF function (2, 20) masks the differences when results are reported in terms of pF.

The relationship between moisture potential and relative moisture content (total moisture percentage/moisture equivalent percentage) is shown, for the entire group of soils, in figure 3.

## INFLUENCE OF MECHANICAL ALTERATION OF STRUCTURE ON FREEZING POINTS

Stirring, mixing, vibrating, or in any way shearing a moist soil generally produces what is termed a "puddled" condition. The violent treatment of the soil aggregates alters the apparent size distribution of the particles, which is intimately connected with the porosity characteristics. Since soil texture has a strong influence upon the freezing point at a given moisture content, it is reasonable to expect that the soil moisture-energy curve will be shifted as the result of an alteration in pore size distribution, and in total porosity. Thomas (29) has demonstrated that this occurs for high energies of retention. The influence of

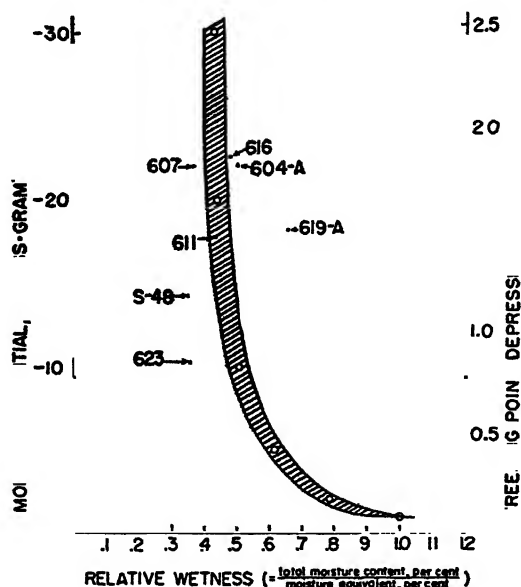


FIG. 3. RELATIONS BETWEEN MOISTURE POTENTIAL AND RELATIVE WETNESS FOR A GROUP OF 14 CALIFORNIA SOILS

The circles represent the moisture potentials plotted against the corresponding mean relative wetnesses. The band shows the standard errors of the moisture contents. The dots show the relations for individual soils at their permanent wilting percentages.

puddling holds special interest in the energy range under investigation, for it is within this range that growing plants obtain their moisture.

Soils were puddled in two different ways, described hereinafter, and subsequently freezing measurements were made. The methods of preparation are designated as methods A and B, respectively.

#### Method A

A 30-gm. sample of air-dry soil was moistened by means of an atomizer to a desired moisture percentage and stored for 1 week in a tightly stoppered bottle. At the end of this time the sample was removed and placed in a glass bell-jar provided with a rubber diaphragm at the large end. By thrusting the arm through a small opening in the diaphragm, the sample could be thoroughly pud-

dled by means of a spatula, without undue loss of moisture. The sample was repeatedly pressed and molded against the side of the jar, with as much shearing motion as possible. After a stated period of puddling, it was removed and placed in the freezing jacket, and a freezing determination was made in the usual way.

TABLE 7  
*Influence of puddling, by method A, upon the freezing point depression of two soils*

DURATION OF TREATMENT	ALTAMONT CLAY (604A)				AIKEN CLAY LOAM (619A)			
	Moisture content	Freezing point depression		Change in freezing point after puddling	Moisture content	Freezing point depression		Change in freezing point after puddling
		Puddled	Unpuddled			Puddled	Unpuddled	
<i>minutes</i>	<i>per cent</i>	<i>°C.</i>	<i>°C.</i>	<i>°C.</i>	<i>per cent</i>	<i>°C.</i>	<i>°C.</i>	<i>°C.</i>
5	26.51	0.185	....		29.26	0.080	....	
5	25.32	0.200	....		28.40	0.100	....	
5	26.03	0.172	....		28.62	0.075	....	
5	26.10	0.203	....		.....	.....	....	
Mean....	25.99	0.190	0.11	-0.08	28.76	0.085	0.08	-0.01
10	26.01	0.203	....		28.68	0.098	....	
10	25.03	0.211	....		28.62	0.113	....	
10	25.04	0.187	....		28.77	0.068	....	
10	25.89	0.223	....		28.21	0.073	....	
Mean....	25.49	0.206	0.13	-0.08	28.57	0.088	0.09	±0
5	18.20	0.514	....		22.45	0.663	....	
5	18.05	0.560	....		22.25	0.835	....	
5	19.16	0.567	....		22.10	0.653	....	
5	.....	.....	....		21.80	0.741	....	
Mean....	18.47	0.547	0.43	-0.12	22.15	0.723	0.73	+0.01
10	16.62	0.669	....		19.98	1.611	....	
10	17.83	0.735	....		20.64	1.400	....	
10	17.21	0.709	....		20.31	1.532	....	
10	17.58	0.707	....		20.71	1.347	....	
Mean....	17.31	0.705	0.58	-0.13	20.41	1.473	1.50	+0.03

Two soils, Altamont clay (604A) and Aiken clay loam (619A), which contain very similar amounts of total clay, were treated in this manner at several moisture contents and for different periods. Comparison is made with the freezing-values for the normal soils in table 7. It is clear that the Altamont soil was significantly altered by the treatments and that the puddled samples showed a greater freezing point depression than the unpuddled samples. The Aiken soil, on the other hand, remained unaffected by the puddling.

The major changes in the freezing point depression of Altamont clay occurred during the first 5 minutes of puddling. An additional 5-minute treatment was

without effect. Assuming that the shift in freezing point depression is due to structural change, the greater part of this change is brought about during the early stages of puddling.

The higher moisture content during the puddling process appears to diminish slightly the effect of the puddling, a somewhat greater depression in freezing point being produced in the drier than in the wetter soil. The average moisture contents were, respectively, 0.67 and 0.93 times the moisture equivalent.

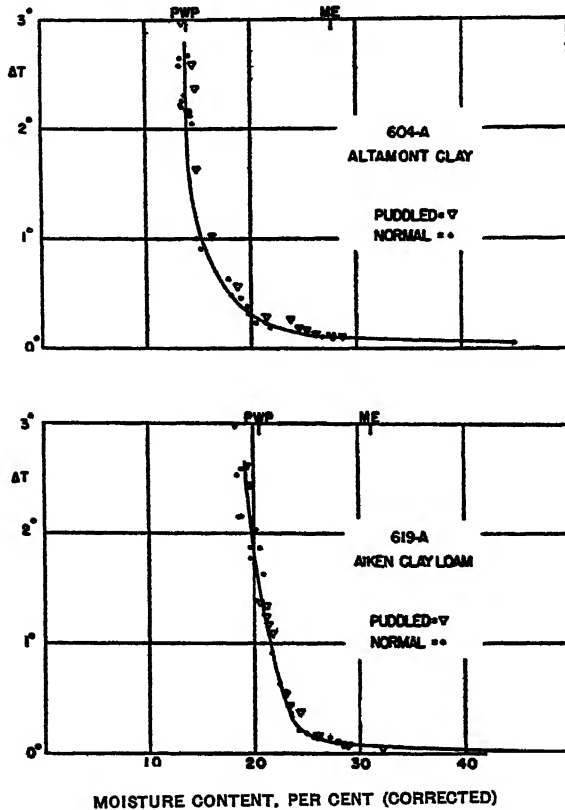


FIG. 4. INFLUENCE OF PUDDLING ON THE FREEZING POINTS OF SOILS

#### Method B

In the second method of puddling, 300-gm. samples of the same two soils were stored for 2 days at moisture contents close to their moisture-equivalent values. They were then removed and puddled continuously with a spatula for 3 hours, with occasional additions of water from the atomizer to keep them near their sticky points. They were dried at room temperature for approximately 1 week, and then gently crushed with a rubber pestle to pass a 2-mm. screen. At this stage it was observed that both soils consisted of very hard angular fragments, quite different in visible structure from the original samples. Each puddled soil, after thorough mixing, was moistened to a series of different moisture con-

tents and then stored for 1 week for subsequent determination of the freezing point. Figure 4 shows the results of these treatments.

The treatment given the soils in method B was probably as severe as would ever be attained in practice and had as its aim violent mechanical dispersion of aggregates. The results are essentially the same as those obtained in method A. The effect on the energy curves was small but significant for the Altamont, and negligible for the Aiken. It is concluded that at these energy levels (between approximately  $-1 \times 10^6$  and  $-18.3 \times 10^6$  ergs per gram) either the pore size distribution has a minor influence upon the moisture potential relative to other factors, or, because of the stability of the microstructure, no great alteration is brought about in the quality of the pores. It appears that structural stability is an especially prominent characteristic of the kaolinitic Aiken clay loam, a conclusion based not only on its behavior in the present case, but also upon other laboratory and field evidence.

In an earlier section, it has been shown that the cryoscopic technique, as well as other methods, indicates that plants growing in *normal* soils show no permanent distress symptoms with regard to their moisture supply until a moisture potential in the range of  $-10 \times 10^6$  to  $-23 \times 10^6$  ergs per gram is reached. In view of work reported by certain other investigators, these results are of particular significance. It has been observed by McGeorge and Breazeale (11) that plants show early symptoms of moisture stress in soils that have been previously puddled. Since in these experiments it has been shown that puddling has so small an effect on the energy curve, it is doubtful whether the resulting harmful effects on plant growth can be attributed to increased energy of retention *per se* on the part of the soil. The results obtained by McGeorge and Breazeale may be explained quite as well on the basis of an increased resistance to root penetration and a reduction in permeability<sup>4</sup> of the soil, caused by the puddling treatments.

#### WATER CONTENT AT CONSTANT MOISTURE POTENTIALS IN RELATION TO CLAY CONTENT AND TO FREEZING POINTS OF EXTRACTED CLAYS

The moisture contents of the soils at moisture potentials between  $-1 \times 10^6$  and  $-30 \times 10^6$  ergs per gram have been obtained from the freezing point depression curves (figure 2) and examined in relation to the corresponding contents of clay finer than  $2 \mu$ . The results are plotted in figure 5, which shows that a distinct correlation exists between clay content and moisture content at a constant moisture potential. This is true for all moisture potentials at which the relationship was examined. It is observed that what may be termed the "clay coefficient" is considerably less at the lower values of  $\mu$  than it is at the higher values. This suggests that factors other than the mere total amount of clay play an increasingly important role as the energy levels of the soil moisture diminish.

The importance of the contribution of the osmotic potential to the moisture potential at the moisture equivalent (average  $\mu = -1.05 \times 10^6$  ergs per gram)

<sup>4</sup> The specific permeability defined in terms of unit potential gradient.

has already been pointed out. The increase in concentration of the soil solution with diminution in water content might be regarded, *per se*, as one possible explanation of the reduced magnitude of the clay coefficient. Examination of the experimental data upon which the curves of figure 5 are based, however, suggests that but little significance can be attached to the solute concentration in this respect. Calculation of the solute concentrations at the various moisture levels, by means of the assumption that an inverse relation exists between concentration and moisture content, shows that of those points lying below the experimental curves for the respective  $\mu$  values, only about one third of the number have solute concentrations in excess of the mean for the group. In

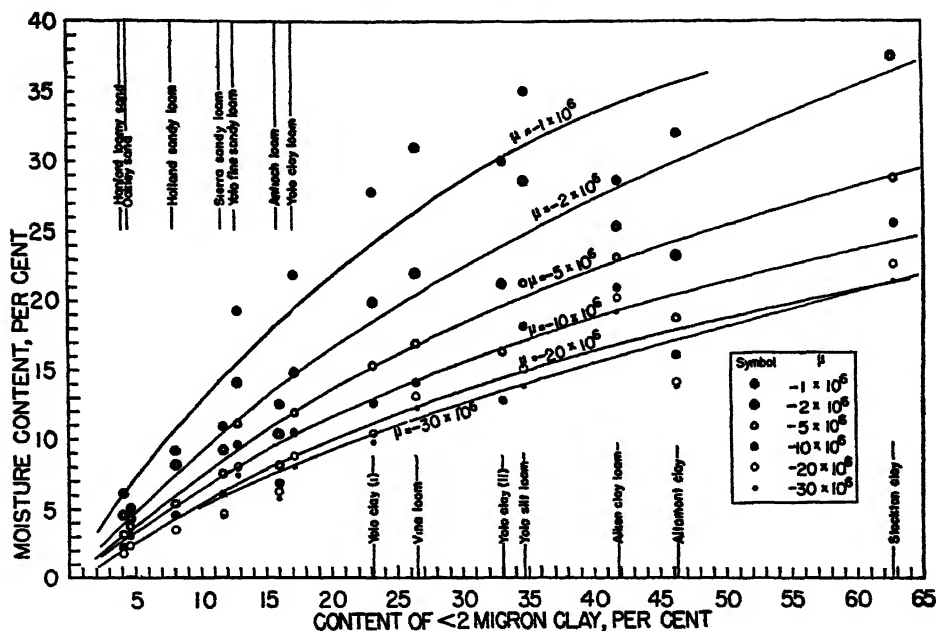


FIG. 5. RELATIONS BETWEEN MOISTURE CONTENT AND CLAY CONTENT AT CONSTANT ENERGY LEVELS OF SOIL WATER

other words, of those soils tending to flatten the curves, those containing solutes in concentrations below the mean somewhat exceed in abundance those having solute concentrations in excess of the mean. Since no information was obtained of the particular differences in ionic distribution between solid and liquid phases of the soils which accompany differences in their moisture content, nothing is known of the corresponding differences in pressure and osmotic potentials and no more exact conclusion can be drawn concerning these influences upon the differences in magnitude of the clay coefficient. That the soil clays undoubtedly exist in a more highly aggregated state, owing to both chemical and mechanical effects, at the lower energy levels than they do at the higher, is probably a contributing factor.

Consideration was given to the possible effect of differences in the mineralogical

character of the colloidal clays themselves upon the freezing point curves of the soils containing them. For this purpose the clays ( $<2 \mu$ ) were extracted by repeatedly stirring 3 per cent aqueous suspensions of separate samples of soil with a motor propeller, allowing them to settle for the necessary time, and decanting between stirrings. The decanted clay suspensions were dewatered by means of a Pasteur-Chamberland filter. Ten decantations were made, and about half the clay was removed from each of seven of the soils in this way. The clays were then air-dried, ground in an agate mortar, passed through a 100-mesh silk sieve, and well mixed. Ten-gram samples were taken for the freezing experiment and moistened, in the same manner as the soils, to a series of suitable moisture contents. In addition to the seven soil clays, two clay minerals, montmorillonite (in the form of "Volclay" bentonite) and a sample of ground kaolinite<sup>5</sup>, were also included in the set for purposes of comparison. The x-ray diffraction patterns of the colloids of six of the soil series here considered have been examined by

TABLE 8  
*Minerals identified by x-ray diffraction in certain extracted clays*

CLAY		KAOLINITE	MONTMORILLONITE	ILLITE	OTHER MINERALS IDENTIFIED	REFERENCE
Number	Name					
	Yolo	None	Predominates	None	Quartz	Kelley et al. (9)
	Vina	Predominates	Trace	None	Quartz	
623	Sierra II	Predominates	Trace	Trace	Quartz, rutile	Perry (16)
626	Holland II	Predominates	None	Present	Quartz	
619	Aiken	Predominates	Trace	....	....	Marshall (12)
613	Stockton	Trace	Predominates	....	....	

Kelley et al. (9), Perry (16), and Marshall (12). It has been emphasized by Kelley and associates that the soil colloids represent a mixture of several mineralogical species, but usually contain a relative abundance of some one predominating clay mineral. Quartz is almost always present in considerable amounts as a supplementary mineral. The list of identified minerals is given in table 8.

Figure 6 contains the freezing data for the clays. The curves lie between those for the soils on the one hand and those for bentonite and kaolinite on the other. When the soil colloids alone are considered, kaolinitic types tend to occur on the left and montmorillonitic types on the right; if, however, the bentonite and kaolinite are taken into account, the position of the freezing curves is more or less independent of the type of predominating mineral species.

The first and most obvious explanation of the results is that the distribution of particle sizes within the clay fraction is of predominating influence on the energy

<sup>5</sup> The bentonite was provided by the American Colloid Company, Chicago. The kaolinite came from the McNamie mine near Langley, South Carolina, and was provided through the kindness of P. R. Stout (27).

curve. The formation of the clay minerals may take place by a synthetic combination of ions in much the same manner as the ordinary processes of crystallization (14). In such cases the particle sizes probably depend upon the conditions of weathering, including the time of exposure, and upon the properties of the particular lattice in process of formation. In other cases the particles may represent residual products of former minerals which have been decomposed by weathering processes. According to the theory of capillarity, the energy curve will depend upon the configuration of the pores, which in turn depends upon the sizes, shapes, and relative positions of the particles. According to multimolecular adsorption concepts, the amount of water retained at a given moisture potential depends upon the amount and nature of the surface accessible to water molecules. Therefore both theories support the prediction that the relative abundance of small and large particles in the colloidal fraction will influence the energy curve.

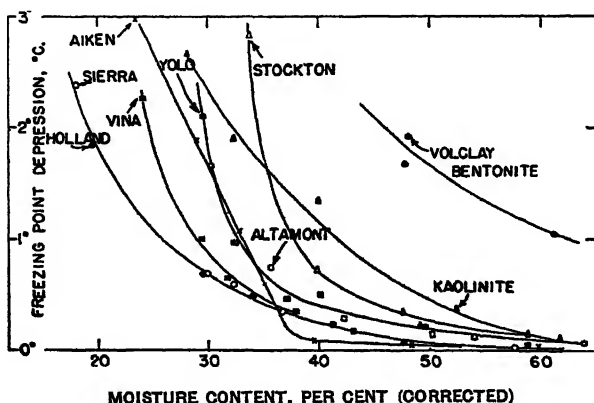


FIG. 6. FREEZING POINTS OF SOIL CLAYS IN RELATION TO THEIR MOISTURE CONTENTS

A second interpretation of the curves depends upon the observation that differences of a fundamental nature, aside from particle size, exist between the constituent colloids of certain of these soil types. Inasmuch as the mechanism of sorption of water in colloidal systems is not yet fully understood, it is not possible, except in a qualitative way, to predict the manner in which these differences affect the moisture potential. According to the theory of capillarity, it can be maintained that the differences in chemical and physical properties of the particles give rise to different structural arrangements and therefore to different energy curves. Multimolecular adsorption theories permit the alternative view that the nature of the surface influences the intensity of retention of moisture directly.

There is striking agreement in two instances between clays extracted from soils of similar parent materials. The Holland and Sierra series, which have been formed by residual weathering under very similar climatic conditions from similar parent materials, give nearly identical energy curves for their extracted clays. The clay of the Altamont series, which is a primary soil derived from sedimentary



rocks in the mountains of the Coast Range, pairs in a similar manner with that of the Yolo series, an alluvial soil derived from the same or similar sources. The Vina series, which is a secondary soil derived by erosion from areas of Aiken soils, does not show as good agreement with the Aiken as does the Yolo with its corresponding residual soil, the Altamont. This may be due to the presence of extraneous material brought in from other sources during the deposition of the Vina soil. It is also to be observed that, where sampled, the two soils now occur under markedly different climatic conditions (table 2). The P-E index of the Aiken is three times as great as that for the Vina, and differences in the predominating kind of weathering, not revealed by the x-ray diffraction patterns, may have been brought about. The results strongly suggest that factors common to soil clays of similar origin give rise to similar energy curves. The processes of erosion and deposition which were responsible for the production of the Yolo soils appear not to have influenced the energy curves of the clays, which, in part at least, were derived from the Altamont soils in more elevated positions.

The factors that give rise to *different* freezing curves of soil clays seem to be of considerable complexity, but it is of importance to note the experimental fact that such differences exist. On the other hand, the data just presented show that certain soil features seem to be associated with energy curves that are *similar*. These similarities might be produced by a balancing of factors; for example, the effects of different surface properties may be balanced by the effects of different particle sizes. Certain regularities seem to exist in spite of such a possible balancing, however, and for this reason considerable significance is attached to the fact that similarities of origin are associated with similarities in the energy curves.

#### SUMMARY

The influences of moisture content, texture, dissolved solutes, constituent clays, and mechanical alteration of structure have been studied with regard to their effects upon the freezing point depression of soils. The corresponding moisture potentials have been calculated by means of the freezing point equation.

The moisture potential at the moisture equivalent is influenced principally by the osmotic effects of dissolved solutes, for the soils investigated; the pressure potential makes a relatively small contribution to the moisture potential at this soil-moisture content.

At the permanent wilting percentage, wide variations were found to exist in the moisture potential from soil to soil. The evidence of this paper suggests that the energy of retention at the permanent wilting percentage is in the order of magnitude of  $-18 \times 10^6$  ergs per gram, corresponding to an equivalent pressure of about 18 atmospheres. This is in general agreement with values reported by other investigators.

Drastic mechanical treatment had only a slight influence on the energy curves. This was attributed to a high degree of stability of the microstructure—an effect especially emphasized in the case of the kaolinitic Aiken soil. Irrespective of the cause, puddling had a rather small effect on the energy curves, and abnormal

moisture deficiencies of plants growing in puddled soils should be attributed to factors other than the intensity of retention of water.

The clay content of the soils, among other influences, affects the moisture content corresponding to a given moisture potential. This influence becomes progressively less as the energy level diminishes. It appears that the higher concentrations of the soil solution, which are necessarily associated with the lower soil moisture contents, are not responsible in themselves, through their osmotic potentials, for masking the effect of the clay.

The different soil clays display widely differing moisture potential curves. The curves for the clays lie between those for the natural soils on the one hand and those for bentonite and kaolinite on the other. Kaolinitic types tend to behave as though they were coarser-grained, though there is no clear-cut relationship between the position of the energy curve and the type of predominating clay mineral present. Soils of related genetic origin tend to show similar energy curves. Unless this is due to a balancing of factors, it appears that the surface properties, extent of surface, and structural configuration are very much the same for colloids from soils of related origin.

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# A SOIL TUBE FOR OBTAINING WET CLAY CORES IN AN UNDISTURBED STRUCTURAL CONDITION

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Certain recent soil moisture investigations at the Blacklands Experimental Watershed Project near Waco, Texas, have required laboratory study of wet, structurally undisturbed samples from a heavy clay soil. The experiments on the areas under investigation do not permit undue disturbance of the soil; consequently, excavation to obtain subsurface samples cannot be resorted to, and since none of the soil tubes and core cutters with which the author is familiar are suitable for obtaining deep, undisturbed samples from a heavy clay soil when in a wet and sticky condition, it was necessary to design and build a special sampling tube.

Many types of tubes and core cutters are described in the literature. The King tube (5) and modifications by Veihmeyer (10) and Harper (4) are well known. Other tubes and core cutters for obtaining soil samples have been devised by Kopp (6), Curry (3), Stevenson (9), Slater and Byers (8), Neller (7), Coile (2), Bradfield (1), and others. All of these require excavation for obtaining subsoil samples, or are in other ways unsuitable for use in a wet, sticky soil.

Efforts to obtain undisturbed cores with tubes having the usual more or less conventional types of cutting heads led to the design of the tube herein described. It is a departure in soil tube design and in the material out of which it is made, but with it satisfactory cores can be obtained from a clay soil when in a moist to very wet condition. In figures 1 and 2 are shown close-up views of the cutting head and of the tube in operation. Sectional views of the cutting head are shown in figure 3.

The cutting head is made of copper. Before the tube is used, the surfaces of the cutting head are thoroughly coated with mercury, both inside and out. This produces a very slick surface, to which the wet clay exhibits but little tendency to stick. A long outside taper and an abrupt increase in bore diameter of approximately  $\frac{3}{8}$  of an inch, taking place as near to the mouth of the tube as the thickness of the walls of the cutting head will safely allow, further reduce the friction between the soil and tube head to the extent that noticeable compression of the core does not occur.

In operation, the tube is forced into the soil with a screw jack. An improvised jack made out of materials on hand at the project is shown in figure 2. The tube

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<sup>2</sup> Blacklands Experimental Watershed Project, Waco, Texas.



FIG. 1

FIG. 2

FIG. 1. CLOSE-UP VIEW OF TUBE CUTTING HEAD

FIG. 2. TUBE IN OPERATION

The screw jack is held in place by soil augers

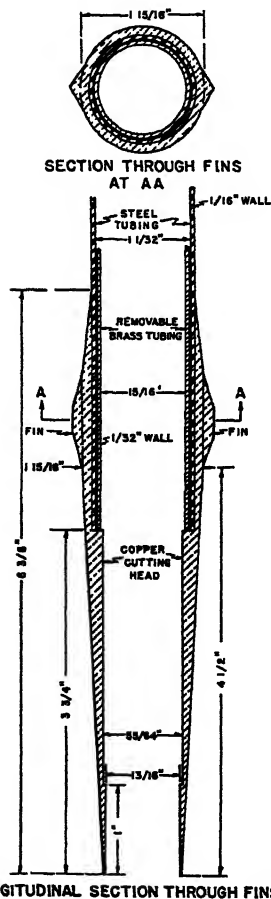


FIG. 3. SECTIONAL DIAGRAM OF THE CUTTING HEAD

is held by hand so as to prevent rotation until the desired depth is reached. It is then given a quarter of a turn before being brought upward. This allows the two grooves in the side walls of the hole, made by the fins in the tube head (fig. 3), to function as passageways by which air can reach the bottom of the hole. Without these air passageways enough suction is created upon bringing up the tube, to pull the core back through the cutting head. The cores are received in removable brass tubes. The part of the core remaining in the bore of the cutting head is pushed into the brass tube with a plunger of the same diameter as the bore of the cutting head. The soil tube is then inverted, and the brass tube and core readily slide out.



FIG. 4. CORES FROM WET HOUSTON BLACK CLAY

Numbers beneath cores designate the approximate soil depths, in inches, from which the cores were obtained

Driving the tube into the soil with a hammer seems to cause some compression of the soil ahead of the tube and often shatters the core as well. It is probable that this compression will occur even when the tube is advanced into the soil with a jack, if advancement is too rapid.

The tube is provided with exchangeable extensions for shallow or deep borings so that the same jack may be used for all depths.

An effort has been made to show pictorially the character of the cores obtainable with this soil tube. Figure 4 gives longitudinal views of the cores from two areas, which were taken when the soil was approximately at its field capacity in moisture content. The soil depth, in inches, from which each sample was taken is given below each core. In obtaining these cores the tube was not always advanced into the soil exactly to the depths indicated; consequently, a comparison of the actual lengths of these cores with the lengths suggested by the depth intervals is not a criterion for determining core compression. Cores from the lower depths are equal in length to the distance which the tube advances

into the soil. Cores from the surface 6 inches, however, generally are  $\frac{1}{2}$  to  $1\frac{1}{2}$  inches shorter than the distance of penetration. This is attributed to the loose structure of the surface soils and to the smallness of the tube diameter. It is recommended that for surface sampling a tube of larger diameter be used. Roots, likewise, tend to disturb the structure of a surface core, since, because of

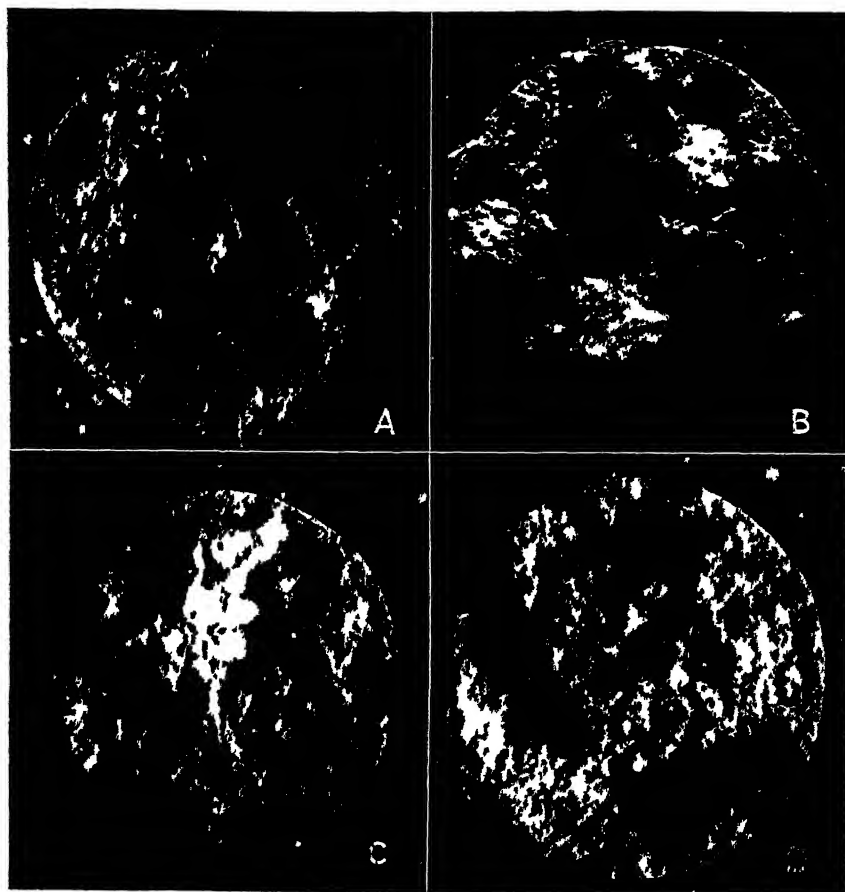


FIG. 5. PHOTOMICROGRAPHS OF CROSS-SECTIONS OF CORES FROM WET HOUSTON BLACK CLAY

Upper left, meadow soil, 2-inch depth, upper right, meadow soil, 6-inch depth; lower left, meadow soil, 48-inch depth; lower right, cultivated soil, 48-inch depth.

Magnification 2.3 to 2.6  $\times$ .

the softness of the material used, the cutting edge may not be sharpened to the degree necessary to cut, without concurrent soil disturbance, all roots that may be encountered.

The total additive lengths of the cores shown in figure 4 are 99.2 and 97.5 per cent of the distance of penetration of the tube into the meadow soil and the cultivated soil, respectively. All of the core compression apparently occurred in the cores from the surface 6 inches.

In figure 5 are shown cross-sectional views of some cores obtained with this tube. Disturbance of structure occurs only for a very small distance inward from the periphery of the core, evident in the photographs as a very thin rim.

It should be pointed out here that because of the softness of the materials used and the slender design of the cutting head, the tube is necessarily limited to use in soils that are free of gravel and tough woody roots, and then only when these soils are in at least a moist condition. A tube with a cutting head made of hardened copper would not be subject to the limitations created by a lack of moisture or the presence of large roots, nor would it be so liable to injury by the encounter of gravel in a soil. It is probable, however, that the ability of copper to amalgamate with mercury may be impaired by the metals used in producing this tough alloy, and that the slick surface which seems so necessary in a tube for obtaining undisturbed cores from a wet clay cannot be obtained. Brass, though harder than copper and readily amalgamable, has the property of becoming brittle when in contact with mercury. It was found unsuitable for use as material for the cutting head.

#### SUMMARY

A description of a new soil tube for obtaining structurally undisturbed cores from a wet clay soil is presented. The cutting head is made of copper and embodies a long slender design, with fins to eliminate suction when the tube is being withdrawn from the soil, and a very slick surface produced by a coating of mercury. Because of the softness of the metal in the cutting head, the tube is necessarily limited to use in a wet soil that is devoid of gravel and large woody roots.

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# THE SWELLING OF QUARTZ SAND, SOIL COLLOID, AND ORGANIC COLLOID<sup>1</sup>

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In a previous study<sup>2</sup> the increased swelling of soils in water resulting from prior treatment with toluene was noted. The present study was extended to include the effect of prior treatment with toluene on the swelling of quartz sand, soil colloid, and colloidal organic matter. From such a study it was thought that the particular soil fraction most responsible for the increased swelling resulting from toluene treatment could be determined, thereby possibly adding to the none too abundant supply of evidence as to the cause of structural stability in soils.

## MATERIALS AND METHODS

Quartz sand was pulverized to pass through a 140-mesh sieve, after which it was treated with concentrated HCl and finally washed free of acid with distilled water. The organic colloid, prepared from partly decomposed alfalfa hay, was from the same supply as that used in a previous study<sup>3</sup> except that it was air-dried and pulverized to pass through a 100-mesh sieve. The soil colloid was isolated from the B horizon of Crete silt loam, after which it was electrodyalyzed, dried, and crushed to pass a 100-mesh sieve.

Swelling measurements were made according to the method outlined previously<sup>4</sup> except that 0.9 gm. of organic colloid was used instead of 2 gm., which was the amount of the mineral samples. The swelling resulting from contact with water alone is reported as that for untreated samples. The tubes containing the samples to be treated with toluene were first stood in toluene for 20 minutes, after which they were immediately transferred to distilled water.

## EXPERIMENTAL RESULTS

The percentage swelling of quartz sand, of the soil colloid, and of the organic colloid when wet with water alone and when previously treated with toluene before placement in water are shown in table 1.

The swelling represents the increase in volume occupied by the solid material after standing in contact with water for 24 hours, expressed as the percentage of the original volume occupied by the air-dry material. The original volumes for

<sup>1</sup> Contribution No. 342, department of agronomy.

<sup>2</sup> Myers, H. E. 1941 Some physicochemical aspects of soil aggregates. *Soil Sci.* 52: 469-480.

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<sup>4</sup> See footnote 2.

any one material were constant, having been so made by moderate jarring of the tubes.

The variation of the number of replicated measurements per type of material used in the experiment was due in part to the quantity of each material available. In all cases the replicate readings were very similar. Although only one reading is reported for the organic colloid, other readings using smaller samples verified the data reported herein.

It was recognized that the increased volume may have been the result of several factors, including (a) the greater affinity of the internal surface of the mass for the liquid, which would influence the thickness of the adsorbed liquid films separating the particles; (b) gaseous occlusions in the system as a result of displaced adsorbed air which might become entrapped; and (c) toluene occlusions that might result as a consequence of its displacement by water. It is believed that actual swelling due to the greater affinity of the mineral particles for water following toluene treatment played an important role. Although occluded gases formed as a result of the displacement of adsorbed air following

TABLE 1

*Swelling of organic and inorganic materials as influenced by prior treatment with toluene*

MATERIAL AND TREATMENT	NUMBER OF SAMPLES	AVERAGE SWELL- ING AFTER 24 HOURS
		<i>per cent</i>
Quartz sand, untreated .....	16	3.8
Quartz sand, toluene 20 minutes .....	16	14.6
Soil colloid, untreated .....	5	55.9
Soil colloid, toluene 20 minutes .....	5	81.8
Alfalfa colloid, untreated .....	1	10.8
Alfalfa colloid, toluene 20 minutes .....	1	4.0

the toluene-water treatment may have contributed to the increased volume, the displaced air probably increased the affinity of the particles for water, which in turn should have increased the thickness of the water film around the particles. The prior toluene treatment greatly increases the wettability of quartz by water. Occluded toluene, as a factor in determining the observed results, was thought to be of little importance because of the ease with which the toluene was displaced by the water, and because the toluene was forced to the surface of the sand by the entrance of water into the system.

The inability of water alone to cause much swelling in quartz sand is in agreement with practical observations. In contrast to this the prior treatment of the sand with toluene brought about a marked increase in the percentage of swelling. Swelling under the latter condition was greater than the average swelling of four normal soils treated only with distilled water. The average swelling of the four soils in water alone was 11.7 per cent,<sup>5</sup> in contrast to 14.6

<sup>5</sup> See footnote 2.

per cent for sand. Obviously the inability of sand to swell appreciably in the presence of water alone cannot be assigned to the absence of an expanding lattice structure. The failure may be more logically explained on the basis of the inability of water to wet completely the surface of the quartz and consequently the inability of the quartz to adsorb strongly the polar molecule, water.

The prior toluene treatment permits more complete wetting of the sand and thereby should make possible greater swelling due to polar adsorption of greater magnitude. The force with which the water is held by the toluene-treated quartz is suggested by the convex meniscus formed by the sand in the glass tube. Since the glass is also thoroughly wet by the water after toluene treatment, it appears that the glass-water-sand system must be very rigid, at least enough so to resist the swelling force which expressed itself to the greatest extent in the center of the sand column.

The differential swelling of the soil colloid with and without toluene treatment is similar to that of quartz sand but of a different order of magnitude. Whether the increase in swelling, due to prior toluene treatment, is lattice or nonlattice swelling cannot be determined from the observations made. Because of the coarser physical state of the quartz sand in comparison to the colloids and of the similarity in swelling in the two systems resulting from toluene treatment, it would appear that much of the additional swelling of the colloid could be the result of nonlattice swelling.

The swelling behavior of the organic colloid is in distinct contrast to that of the soil colloid and the quartz sand. Prior toluene treatment reduced the swelling of the organic colloid in water over that of water alone.

If the behavior of the organic fraction of the soil in relation to toluene is similar to that of the organic colloid used in this experiment, then such behavior suggests that the organic fraction of the soil does not exist as a complete covering over the mineral fraction. It was previously shown<sup>6</sup> that the toluene treatment of soils resulted in an increase in the degree of swelling rather than a decrease, as shown by the isolated organic colloid. The increase in swelling due to the toluene treatment appears then to be associated with the mineral surfaces free of organic matter.

<sup>6</sup> See footnote 2.



# EFFECT OF TYPE OF CLAY MINERAL ON THE UPTAKE OF ZINC AND POTASSIUM BY BARLEY ROOTS

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A significant trend of experimentation in the field of mineral nutrition of plants is based on the belief that the customary water culture techniques provide adequate means for the study of the effects of various combinations of electrolytes on plant growth in soils. Though this approach has been satisfactory for coarse-textured soils, its application to fine-textured soils encounters serious difficulties because of the presence of colloidal clay particles. The concept of the diffuse electric double layer and observable phenomena such as the suspension effect (10) and the contact effect (5) point to the fact that the activities of the ions in colloidal systems are in large measure dependent on the properties of the colloidal particles themselves. Considerations of this kind focus attention on the influence of the soil colloids, particularly their size and shape and the properties of their surfaces, on the mineral nutrition of plants in soils.

In the present paper are reported certain studies of the effect of the type of clay on the uptake of adsorbed zinc and potassium by barley roots. The investigation comprises montmorillonitic and kaolinitic clays, which are important constituents of many soils and which differ fundamentally in their crystal structure (1).

## ZINC UPTAKE FROM ZN-BENTONITE AND ZN-KAOLINITE

Na-bentonite and ground Na-kaolinite were converted into zinc clays by leaching with normal solutions of Zn-acetate having a pH of 6.4. Excess acetate was removed with a 50 per cent solution of methyl alcohol. The amount of exchangeable zinc on the clays was determined by leaching the materials with normal, neutral ammonium acetate. The leachate was analyzed for zinc by means of the polarographic method (9). The amount of exchangeable zinc, expressed as divalent zinc, was found to be 120 m.e. per 100 gm. for the bentonite clay, and 22 m.e. per 100 gm. for the kaolinite clay.

Six very dilute clay suspensions were prepared containing 0.05, 0.25, and 1.00 m.e. of exchangeable zinc as Zn-bentonite and Zn-kaolinite in 3 liters of distilled water. To each container was added 70 gm. of fresh, excised barley roots obtained according to the method of Hoagland and Broyer (4). The roots were left in the suspensions for 8 hours. During this time the sols were continuously aerated and frequently stirred in order to prevent settling of the mineral particles. The initial pH values of the clay suspensions varied between 6.91 and 7.19. At the end of the experiment the pH range was between 6.26 and 6.60. After the roots had been carefully and thoroughly rinsed in distilled water they were dried, ashed, and analyzed for zinc according to the dithizone method (3). An aliquot

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of the original roots, after immersion in distilled water for 8 hours, had a zinc content of 1.00 mgm. per 70 gm. of fresh roots. This value was subtracted from the test roots.

The amount of zinc taken up by the active roots as a function of zinc concentration and type of clay is shown graphically in figure 1. The shape of the curves is typical of nutrient absorption of living roots. Noteworthy is the fact that the roots obtained more zinc from Zn-bentonite than from Zn-kaolinite. This holds true for all zinc concentrations investigated. The difference is greatest at low concentrations, where it amounts to over 90 per cent. These experiments were repeated in June and in August and in every instance more zinc was taken up from bentonite than from kaolinite.

#### POTASSIUM UPTAKE FROM K-BENTONITE AND K-KAOLINITE

Potassium clays, obtained by the potassium acetate method, contained 73.5 m.e. of exchangeable K per 100 gm. oven-dry material for K-bentonite and 15.4 m.e. of K for K-kaolinite. K-bentonite and K-kaolinite sols were prepared having concentrations of 0.50, 1.00, 2.50, and 5.00 m.e. of exchangeable K in 3 liters. Some of these suspensions were fairly concentrated. For example, the systems having 5 m.e. of exchangeable K corresponded to a 3.3 per cent bentonite sol and a 10.8 per cent kaolinite sol.

To each jar was added 60 gm. of fresh barley roots weighing 4.81 gm. when oven-dried, and containing 45.2 m.e. of K per 100 gm. oven-dry weight. The systems were aerated and stirred for 8 hours. Then the roots were removed from the containers, washed, and analyzed for K by the cobaltinitrite method (2).

The uptake of K from the various clay sols is shown in figure 2. The curves representing these K-systems are in substantial agreement with the data obtained with zinc clays. Again the roots tended to accumulate more cations from bentonite than from kaolinite, though the total amounts of exchangeable potassium were identical in the two series. The difference in behavior of the two clays is more pronounced at low concentrations, where the K-uptake from bentonite exceeds that from kaolinite by 90 to 100 per cent. At higher K concentrations bentonite and kaolinite behave alike. This range corresponds to the maximum absorption rate of the roots under the conditions of the experiment.

It is of interest to compare the pH changes that have occurred in the two clay systems. Initially, the pH values of the bentonite and kaolinite sols were nearly identical, being 7.52 and 7.40, respectively, at the lowest concentration, and 8.12 and 8.15, respectively, at the highest concentration. At the end of the experiment all systems were acid. The pH values of the bentonite sols varied from 4.41 to 5.40, whereas those of the kaolinite sols ranged from 5.62 to 6.38. The amount of titrable acidity (exchangeable H-ions) was considerable and in some of the systems was comparable to the amount of potassium taken up by the roots. The significance of these reaction changes will be discussed in one of the subsequent sections.

An experiment performed in May included 85 gm. of fresh roots in 3 liters of suspensions containing 2.00 m.e. of K. Calculated on a 100-gm. basis, the roots

removed 1.93 m.e. of K from K-bentonite and 1.38 m.e. of K from K-kaolinite. This experiment was repeated in June, with 80 gm. of fresh roots. The uptake (100 gm. roots) from bentonite was 1.93 m.e. of K; from kaolinite it was 1.32 m.e. The absolute, and especially the relative, agreement between these experiments is representative of the reliability of the technique employed in these studies.

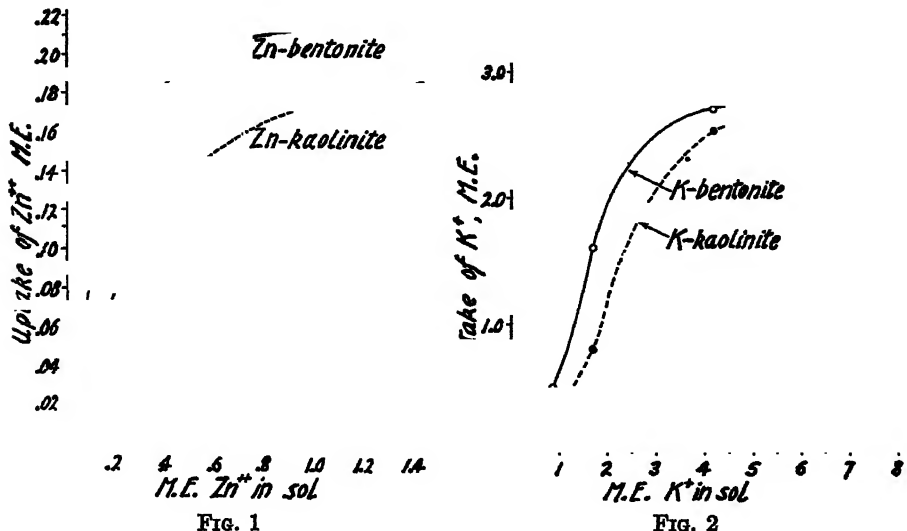


FIG. 1. UPTAKE OF ZINC FROM Zn-BENTONITE AND Zn-KAOLINITE BY EXCISED BARLEY ROOTS (JULY)

All values on the axes refer to 100 gm. of fresh roots in 4.28 liters of sol

FIG. 2. UPTAKE OF POTASSIUM FROM K-BENTONITE AND K-KAOLINITE BY EXCISED BARLEY ROOTS (OCTOBER)

All values on the axes refer to 100 gm. of fresh roots in 5 liters of sol

TABLE 1

*Uptake of K from K-Yolo silt loam and K-Aiken clay by excised barley roots*  
(Milliequivalents K per 100 gm. of fresh roots in 5.45 liters of suspension)

SOIL	EXCHANGEABLE K IN SOILS	K UPTAKE BY ROOTS
	m.e.	m.e.
K-Yolo.....	1.36	1.32
K-Aiken.....	1.36	0.88
K-Yolo.....	2.27	2.23
K-Aiken.....	2.27	1.78

#### POTASSIUM UPTAKE FROM K-YOLO SILT LOAM AND K-AIKEN CLAY SUSPENSIONS

Samples of Yolo silt loam and Aiken clay soils were converted into K-soils by the acetate method. One hundred grams of K-Yolo silt loam contained 24.6 m.e. of exchangeable K. The corresponding value of the K-Aiken clay was 19.4. Suspensions of Yolo soils and of Aiken soils were prepared containing 0.75 and



1.25 m.e. of K in 3 liters. To each jar was added 55 gm. of fresh barley roots. The systems were then treated as described in the preceding sections.

The magnitudes of the K-uptake from these soil suspensions are given in table 1. From the K-Yolo soil the roots took up nearly all of the exchangeable K present. Potassium held on Aiken clay is definitely less available than K adsorbed on Yolo silt loam. These data assume special significance when it is recalled that the Yolo soils are rich in montmorillonitic clay minerals (6), whereas the Aiken soils possess a preponderance of kaolinitic minerals. In other words, the behavior of these two soils fully corroborates the observations made with bentonitic (montmorillonitic) and kaolinitic clays.

#### INADEQUACY OF THE $\text{CO}_2$ THEORY

As has been indicated, all the clays studied become acid under the influence of the living plant roots. A substantial amount of the K removed from the clay is replaced by hydrogen ions. This is in harmony with the prevailing  $\text{CO}_2$  theory of plant nutrition in soils (7, 8), according to which carbonic acid excreted by roots is responsible for the release of adsorbed potassium. In order to account for the differences in K-uptake from the two clays investigated, it is only necessary to assume that carbonic acid releases more K from bentonite than from kaolinite. This assumption was tested by subjecting the Zn-clays and K-clays to equilibrium exchange studies with hydrogen ions derived from water, carbonic acid, and hydrochloric acid.

Amounts of Zn-bentonite and Zn-kaolinite corresponding to 0.60 m.e. of  $\text{Zn}^{++}$  were suspended in 100 cc. of solution containing 0.60 m.e. *hydrochloric acid*. After 48 hours, when equilibrium had been reached, the suspensions were centrifuged in a McBain spinning top centrifuge. The zinc content of the clear supernatant liquid was determined by the polarographic method. Hydrochloric acid freed 45.0 per cent of  $\text{Zn}^{++}$  from Zn-bentonite and 70.1 per cent  $\text{Zn}^{++}$  from kaolinite. It is to be noted that in contrast to the availability curves (fig. 1) the behavior of the two types of clay is reversed; hydrogen ions replace more zinc from kaolinite than from bentonite. These chemical equilibrium data are in harmony with the acidic properties of the two clay minerals. As judged by titration curves of H-clays with bases, kaolinite is a weaker acidoid than bentonite. Consequently, base-saturated kaolinite has a higher affinity for  $\text{H}^+$  than has base-saturated bentonite.

The replacement studies involving hydrochloric acid were extended to K-clays. At  $1S^2$  concentration of HCl, 71.1 per cent of the K was released from K-bentonite and 83.5 per cent from K-kaolinite. Clearly, potassium and zinc behave in a similar manner as regards their relative degrees of liberation from the two clays.

In order to approach actual soil conditions more closely, the release of zinc and potassium was also determined in suspensions containing various amounts of *carbonic acid*. Distilled water in equilibrium with the  $\text{CO}_2$ -pressure of the atmos-

<sup>2</sup>  $S$  denotes the amount of electrolyte added in terms of the saturation capacity of the suspension.

phere has a low concentration of  $\text{CO}_2$  (0.00054 gm. per liter, at  $18^\circ\text{C}$ ). The release of K is brought about mainly by hydrogen ions of water (hydrolysis). Water saturated with  $\text{CO}_2$  has a pH of about 4.0 and contains 1.79 gm. of  $\text{CO}_2$  in 1 liter at  $18^\circ\text{C}$ .

According to the data presented in table 2 the results obtained with the carbonic acid systems are in full accord with those of the HCl systems. In every case the hydrogen ions replace more bases from kaolinite than from bentonite.

Comparison of the behavior of the adsorbed ions in equilibrium exchange, on the one hand, and in the accumulation process by plant roots, on the other, casts doubt on the validity of the  $\text{CO}_2$  theory in explaining the mineral nutrition of plants in the two clay systems. Let us express the reaction between  $\text{CO}_2$  and K-clay in the following manner:

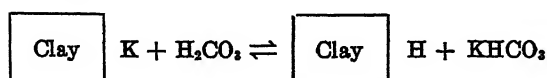


TABLE 2  
*Release of exchangeable bases by carbonic acid and hydrochloric acid*

SYSTEM	CONCENTRATION OF CATION PER LITER	RELEASE OF EXCHANGEABLE BASES		
		Hydrolysis	Saturated $\text{CO}_2$	1 <i>N</i> HCl
	<i>m.s.</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Zn-bentonite.....	8.8	....	5.9	45.0
Zn-kaolinite.....	8.8	....	10.7	70.1
K-bentonite.....	0.67	....	40.1	71.1
K-kaolinite.....	0.67	....	64.6	83.5
K-Yolo soil.....	0.25	15.3	76.0	....
K-Aiken soil.....	0.25	27.6	84.0	....

In applying this equation to the problem of cation uptake by roots, we must consider the amounts of  $\text{KHCO}_3$  in solution, which, according to the soil solution theories, are the only immediate source of K for utilization by the plant. We know definitely that carbonic acid replaces more K from kaolinite than from bentonite, and indeed, the kaolinite sol is always found to be richer in dissolved potassium than the bentonite sol. Hence, the  $\text{CO}_2$  theory in its present form would predict that roots should favor accumulations of K from kaolinite suspensions. This is not in harmony with the observed facts. Probably some sort of contact effect comes into play that requires modification or even abandonment of the current, simple  $\text{CO}_2$  theory.

#### LIMITED SIGNIFICANCE OF FREE ELECTROLYTES

Many soils, especially those of arid regions may contain, at times, appreciable amounts of nitrates dissolved in the soil solution. The nitrate anions are accompanied by dissolved cations. It is conceivable that these free electrolytes may

overshadow the direct influence of the nature of the colloidal particles on the mineral uptake by plant roots. Interestingly enough, experiments show that this need not necessarily be the case.

The aforementioned experiments with K-Yolo soil and K-Aiken soil were also conducted in the presence of  $\text{NaNO}_3$ . To the systems described in table 1 were added 0.1S and 1S concentrations of  $\text{NaNO}_3$ . In terms of amounts of oven-dry Yolo soil these additions correspond to 344 and 3,440 p.p.m. of N. At field capacity Yolo silt loam contains about 26 per cent water; therefore, the calculated nitrate concentration of the soil solution is at least 13,200 p.p.m. N for the soil receiving 1S  $\text{NaNO}_3$ . Under the conditions of the experiment soil and nitrate were diluted to a volume of 3 liters. The actual nitrate concentration (1S) was therefore 5.8 p.p.m. of nitrogen. This dilution favors the release of adsorbed K by  $\text{NaNO}_3$ , by hydrolysis, and by carbonic acid.

According to table 3, the combined effect of hydrolysis and base exchange involving Na has replaced from 40 to 50 per cent of the exchangeable K, which in every case is greater for the Aiken than for the Yolo soil. Nevertheless, the roots

TABLE 3

*Uptake of K by excised barley roots in presence of  $\text{NaNO}_3$*   
(All values relate to 100 gm. of fresh roots in 5.45 liters of suspension)

SOIL	EXCHANGEABLE K IN SOILS	$\text{NaNO}_3$ ADDED	K IN SOLUTION (SUPERNATANT LIQUID)		K UPTAKE BY ROOTS
	m.e.	m.e.	m.e.	per cent	m.e.
K-Yolo .....	1.36	0.136	0.53	39.0	1.12
K-Aiken .....	1.36	0.136	0.67	49.3	0.90
K-Yolo .....	2.27	2.27	0.91	40.1	2.19
K-Aiken .....	2.27	2.27	1.04	45.8	1.73

accumulate substantially more K from Yolo silt loam than from Aiken clay. In other words, the presence of  $\text{NaNO}_3$  and the subsequent release of K have been unable to overcome the specific action of the clay particles on the uptake of K.

#### SUMMARY

Zinc and potassium ions adsorbed on clay particles are readily utilized by excised barley roots. Under comparable experimental conditions, the roots tend to remove more cations from bentonite sols than from kaolinite sols. This is especially true for low concentrations of cations. At higher concentrations no difference was found.

The same behavior was observed with suspensions of Yolo silt loam and Aiken clay. The former contains montmorillonitic clay, the latter, kaolinitic clay.

These findings cannot be explained by the current  $\text{CO}_2$  theory and soil solution concepts, for hydrolysis, carbonic acid, and  $\text{NaNO}_3$  bring about a greater release of cations from kaolinite than from bentonite. Some additional factor, not yet fully evaluated, but associated with the nature of the colloidal clay, comes into play.

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# SOIL DEVELOPMENT AND PLANT NUTRITION: II. MINERALOGICAL AND CHEMICAL COMPOSITION OF SAND AND SILT SEPARATES IN RELATION TO THE GROWTH AND CHEMICAL COMPOSITION OF SOYBEANS<sup>1</sup>

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The sand and silt separates of the soil have not commonly been accorded importance in determining the immediate growth and composition of plants. A recent study (6), which used electrodyalyzed acid clay mixed with sands and silts as a growth medium, demonstrated that this clay fraction served to decompose the mineral soil particles of coarser texture (much as minerals are weathered naturally) for the nourishment of plants. This suggested the chemical action of a standardized hydrogen clay admixed with sands and silts and the later plant growth on such a substrate as a test of plant nutrient delivery from these supposedly less active soil separates as related to their mineralogical and chemical compositions. The results of such tests of silts and sands<sup>3</sup> separated from soils of different degrees of development in different parts of the United States are reported herewith.

## PLAN AND PROCEDURE

The method of preparing the sand-silt-clay substrates for growing soybean plants was the same as that previously used (6). After the plants had grown for 6 weeks they were removed, dried in the oven, and weighed, and a sample was digested with  $\text{HNO}_3$  and  $\text{HClO}_4$ . The digestate was analyzed for calcium, magnesium, potassium, and phosphorus. Nitrogen determinations were made by the standard Kjeldahl procedure.

The sands and the silts were analyzed both mineralogically and chemically. A chemical determination was made of the quartz residue and of the total calcium as follows: A 0.5-gm. sample was treated in a platinum evaporating dish with 10 ml. of 25-30 per cent  $\text{H}_2\text{SiF}_6$  in a constant temperature chamber at  $25^\circ\text{C}$ . for 24 hours. Water was then added, the quartz residue filtered off, dried at  $110^\circ\text{C}$ ., and weighed. The evaporated filtrate was treated with  $\text{HNO}_3$ , taken up with water, and its calcium content determined.

The mineralogical analyses were made by means of the heavy liquid technique. Tetrabromomethane with a specific gravity of 2.90 was used alone, and a specific mixture of it with nitrobenzene to provide a liquid with a specific gravity of 2.68. A 1-gm. sample of the sand-silt minerals was first put on the surface of the latter liquid in a tube and centrifuged to throw down the fractions of greater density.

<sup>1</sup> Contribution from the department of soils, Missouri Agricultural Experiment Station Journal Series No. 868.

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<sup>3</sup> The range in dimensions as effective diameters was 1 to 0.005 mm.

After this separation the fractions of lesser and greater densities than 2.68 were washed in alcohol, dried, and weighed. The heavier fraction was carried through a similar procedure using the liquid with a specific gravity of 2.90. Those minerals with specific gravities falling between 2.68 and 2.90 were considered the "heavy feldspars," and those beyond 2.90, the "heavy minerals."

Quartz grains with inclusions of heavy minerals came down with the heavy feldspars in many samples. In such cases correction was made by determining the percentage of quartz. Since all the heavy feldspars have refractive indexes greater than 1.550 and quartz omega is 1.554, the percentage of quartz falling with the heavy feldspar group was determined by placing the sample in an immersion oil with an index of 1.550 and examining it under the petrographic microscope.

The difference in chemical composition of the soybean plants and of the seeds planted indicated the nutrient elements contributed by the sands and silts through interaction with acid clay, which of itself contributes little of nutrients (1). It was thus possible to measure the relative values of these fractions in soils in the different geographic locations represented.

#### EXPERIMENTAL RESULTS

##### *Chemical composition of soybean plants*

*Nitrogen fixation.* By comparison of the amount of nitrogen in the seed planted (315 mgm.) with that in the harvested crops, as given in table 1, it is evident that on the sands and silts from North Dakota, Iowa subsoil, Iowa surface, and Utah, each mixed with acid clay, the plants fixed nitrogen. On the coarse separates from Missouri, Mississippi, Kansas, and southern Illinois, or on quartz sand and silt interacting with the acid clay, the plants failed to fix nitrogen.

These results suggest that the plants were not obtaining their mineral requisites for a growth that represented nitrogen fixation in this latter group of more southern and eastern states with higher rainfall and higher temperatures. In the former group of states with less severe forces for soil development, the plants obtained their needed mineral supply for growth and nitrogen fixation.

*Calcium and magnesium.* More calcium was found in the plants than was originally present in the seeds in all cultures that grew well enough to be harvested. This points clearly to the movement of calcium from the sand and silt minerals to the plants by way of the acid clay, which of its own breakdown delivered no calcium (1). Accordingly, the sands and silts from Missouri, Mississippi, and southern Illinois soils were failing to deliver calcium to make growth possible.

All the cultures that grew well enough to be harvested, except those using sand and silt from the Iowa surface soil, contained more magnesium than was in the planted seeds. Magnesium then, too, was moving from the sands and silts to the plants by means of the acid clay in sufficient quantities and rates to support growth for the period represented.

*Potassium and phosphorus.* Only the sands and silts from North Dakota produced plants that contained potassium significantly in excess of that originally in the seed. For those from Iowa subsoil and from Utah, the crop content of potassium was about the seed equivalent. In the other cases the crops contained less potassium than the seeds offered, suggesting the movement of potassium from the plant to the hydrogen clay (3, 7).

Only the cultures on sands and silts from Utah suggest removal of phosphorus from the substrate; those from Iowa suggest neither loss nor gain in phosphorus; and the other cultures analyzed suggest losses of this nutrient.

TABLE 1

*Crop weights and chemical composition of soybeans as influenced by different sand and silt separates in acid clay*

SOURCE OF SAND AND SILT SEPARATES*	TOTAL CROP WEIGHT (50 PLANTS)	COMPOSITION OF PLANTS†									
		Nitrogen		Calcium		Magnesium		Potassium		Phosphorus	
		gm.	per cent	mgm.	per cent	mgm.	per cent	mgm.	per cent	mgm.	per cent
North Dakota (Barnes) . . . . .	9.98	3.19	318	0.49	49	.19	19	1.03	102	.29	29
Iowa subsoil (Clarion) . . . . .	24.47	2.10	514	1.12	273	.63	154	0.34	83	.13	32
Iowa surface (Clarion) . . . . .	16.39	2.49	408	0.25	41	.05	8.5	0.25	41	.06	10
Missouri (Putnam) . . . . .	‡	...	...	...	...	...	...	...	...	...	...
Mississippi (Lufkin) . . . . .	‡	...	...	...	...	...	...	...	...	...	...
Utah (Hyrum) . . . . .	18.37	2.52	463	0.94	173	.19	35	0.44	81	.19	35
Kansas (Hays) . . . . .	6.61	3.64	244	0.41	28	.23	15.5	1.06	71	.31	21
Southern Illinois (Cisne) . . . . .	‡	...	...	...	...	...	...	...	...	...	...
Quartz . . . . .	‡	...	...	...	...	...	...	...	...	...	...

\* With each location is given the name of the soil series used. In most cases the type was a silt loam.

† Fifty soybean seeds contained 315 mgm. nitrogen; 8.1 mgm. calcium; 10.8 mgm. magnesium; 80 mgm. potassium; and 32.0 mgm. phosphorus.

‡ The plants on the separates from Missouri, Mississippi, southern Illinois and on the quartz sand grew so poorly that they could not be harvested.

### *Chemical composition of silt separates*

The quartz and calcium contents of the silts were next determined. The data are assembled in table 2.

The insoluble quartz varies widely, from a maximum of 87.8 per cent in the silt from Mississippi, the southernmost sample, to a minimum of 43.3 per cent in that from the Iowa subsoil. The calcium contents of the silts vary less in absolute values than the quartz, but more relatively. The silt from Mississippi, which was highest in quartz, was the lowest in calcium; and the Iowa subsoil, which was lowest in quartz, was the highest in calcium. It does not follow from the remainder of the cases, however, that there is an inverse relation between the calcium and the quartz contents of the silts.

Since these silts were not analyzed for magnesium, potassium, and phosphorus, the more complete delivery of all these nutrients to the plants from the



silts can not be related to the chemical composition of the mineral. Plant composition suggests, however, that the silts from the Iowa subsoil and from Utah were allowing the calcium, magnesium, potassium, and phosphorus to be provided for the plants; or certainly they were saturating the clay well enough with

TABLE 2  
*Quartz residues and calcium contents of the silt separates*

SOURCE OF SILT SEPARATE*	INSOLUBLE QUARTZ	CALCIUM
	<i>per cent</i>	<i>per cent</i>
North Dakota (Barnes).....	70.2	0.90
Iowa subsoil (Clarion).....	43.3	1.10
Iowa surface (Clarion).....	66.6	0.70
Missouri (Putnam).....	73.0	0.50
Mississippi (Lufkin).....	87.8	0.25
Utah (Hyrum).....	75.0	0.48
Kansas (Hays).....	68.8	0.64
Southern Illinois (Cisne).....	73.2	0.40
Quartz.....	98.0	0.00

\* With each location is given the name of the soil series used.

TABLE 3  
*Mineral composition of the sand and silt separates*

SOURCE OF SAND AND SILT SEPARATES	LIGHT FELDSPARS* SP. GR. <2.68	QUARTZ RESIDUE	HEAVY FELDSPARS† SP. GR. >2.68		HEAVY MINERALS‡ SP. GR. >2.90	
	Silt§	Silt§	Silt	Sand	Silt	Sand
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
North Dakota (Barnes).....	27.0	70.2	1.5	0.3	0.9	1.5
Iowa subsoil (Clarion).....	29.0	43.3	13.0	5.0	0.9	1.7
Iowa surface (Clarion).....	29.0	66.6	1.4	2.4	1.4	1.3
Missouri (Putnam).....	26.4	73.0	0.2	0.2	0.4	1.6
Mississippi (Lufkin).....	11.7	87.8	0.1	0.0	0.4	0.8
Utah (Hyrum).....	21.6	75.0	2.9	0.6	0.4	1.2
Kansas (Hays).....	29.6	68.8	0.5	0.6	1.1	2.9
Southern Illinois (Cisne)....	24.7	73.2	0.4	0.1	1.7	0.7

\* May contain microcline, orthoclase, albite, oligoclase, and andesine.

† May contain labradorite, bytownite, or anorthite.

‡ Zircon, hornblende, garnet, tourmaline, kyanite, pyroxenes, Fe-minerals, magnetite, etc.

§ Percentages of light feldspars and of quartz residue in sand separates not determined.

some, if not many, of the nutrient elements measured, so that these were not moving in reverse, or going from the plants to the hydrogen clay.

Only a more detailed study will permit the chemical balance to more accurate degrees, but it is interesting to note that these two cultures with the highest movements of calcium into the crops, and with the absence of deficiencies in magnesium, potassium, and phosphorus, according to plant composition (table 1),

represent in the one case a silt high in calcium (1.10 per cent) in the Iowa subsoil, and in the other case a silt relatively low in calcium (0.48 per cent) in the Utah soil. All of these facts emphasize the importance of having no limiting supplies of nutrients if plant growth is to be significant.

#### *Mineralogical properties of sand and silt separates*

Since quartz is an increasing part of the soil as it weathers under some conditions, and since heavy minerals also accumulate as a part of the residue in the natural weathering processes, the mineralogical properties of the silts were tabulated as a result of petrographic microscopic examinations, coupled with the results of the chemical and physical studies. Table 3 gives the mineral compositions of the various separates.

#### DISCUSSION

##### *Nutrients contributed by sand and silt separates*

The fact that calcium increased over that in the seed in all the cultures making significant growth shows that the sands and silts were contributing this nutrient, either through direct root contact with the minerals or through root contact with the acid clay, the hydrogen ion of which was exchanging with the cation calcium of the minerals and decomposing them in a manner simulating what is commonly considered the weathering process (5). These interpretations are in accord with the work of Albrecht and Jenny (2), showing that plants damped-off unless sufficient calcium was available. On the sands and silts that failed to produce harvestable crops in these trials, symptoms of damping-off were common. These observations suggest that the content of calcium-bearing minerals was too low to respond rapidly enough to the action of either the plant roots or the acid clay to provide calcium for healthy growth of the soybeans.

Like calcium, to which it is chemically similar in many respects, magnesium is mobilized out of the minerals from the same soils, with the exception of the Iowa surface soil, by the acid clay for plant nourishment. The acid clay apparently is what might be termed a "weathering agency" with respect to the breakdown of the magnesium-bearing minerals, including the ferro-magnesium minerals (4).

Though potassium was present in large amounts in the minerals of the sands and silts used in these tests, this nutrient was not so freely moved into the plants as were calcium and magnesium. As has been previously suggested (4), potassium seems to be mobilized out of its minerals with relative slowness by the acid clay.

The phosphorus mobilization was also relatively insignificant as indicated by plant growth and composition. This may have resulted either because there were too few phosphorus-bearing minerals, or because the hydrogen clay was not sufficiently active in decomposing them to provide effective phosphorus. The former seems the more plausible, since rock phosphate, an insoluble form, has given soluble phosphorus when treated with hydrogen clay.<sup>4</sup>

<sup>4</sup> Unpublished data by E. R. Graham et al.

That nitrogen fixation occurred, is evidence of fairly general provision of all the requisite nutrients. When the soybean crop on the silts and sands of the Iowa subsoil fixes enough nitrogen to represent an increase of 63 per cent over that provided by seed and substrate, one scarcely expects nutrient deficiencies in the soil growing the crop. When the acid clay alone is scarcely a better growing medium than quartz, there is strong indication of the cationic movement from the mineral silts and sands to the plants because of the acid clay action on these mineral separates. That the plants failed to fix nitrogen in certain sands and silts indicates that these separates were deficient in some nutrients, including possibly calcium and magnesium as well as those elements that failed to increase in the tissues as the plants developed.

#### *Quartz content of soil minerals in relation to plant growth*

Casual examination of the mineralogical and chemical analyses of the sands and silts as related to plant composition might lead one to believe that poor plant growth is correlated with a high quartz content of soil minerals. This conclusion might be drawn from the fact that the Iowa subsoil with best plant growth had the minimum quartz content, whereas the Mississippi soil with poorest crops had the maximum quartz content. Other data, however, show this conclusion unsound. The Utah minerals with 75 per cent quartz, a figure not far below that for Mississippi, were highly effective in providing plant nourishment. Those from Missouri and southern Illinois contained less quartz but failed to grow the plants, suggesting that, even with a significant store of minerals other than quartz, these were not providing the necessary nutrients through the action of the acid clay.

#### *Heavy feldspars as a fertility index*

The heavy feldspar content of the sands and silts (table 3) appears to be related to the crop growth and to the total amount of calcium removed by the plants (table 1) in these trials. Further studies are needed to determine whether this correlation is as highly reliable as these limited data indicate.

#### *Calcium feldspars as an index of soil development*

In contact with hydrogen clay, the calcium feldspars break down much more rapidly than the potassium feldspars (4). Consequently, if a soil contains no highly calcareous feldspars, it has apparently developed far enough in the weathering process, which is considered similar to that of the action of the acid clay, that the soil minerals will release nutrients slowly to plants and potassium may be the main nutrient left to be released. The low percentage of the calcium feldspars may be an index of the high degree of development of the soils in the humid region and may be associated with the lime need of these soils for production of the calcophilous legumes.

#### *Mineral contents of sand and silt separates in soil classification*

Soil classifications involving the criterion of productivity seem more feasible if attention is given to the mineralogical contents of the soils. If the quartz

residue, the light feldspar fraction (containing microcline, orthoclase, and the plagioclase series from albite to oligoclase), the heavy feldspar fraction (containing andesine and anorthite) in the plagioclase series, and the ferro-magnesium minerals of the heavy mineral fraction were included, considerable value in terms of productivity could be assessed, particularly of the heavy feldspar fraction for its calcium and of the amphiboles and pyroxenes for their magnesium. Relationships of cation fertility to mineral composition are suggested in table 4.

TABLE 4

*Mineralogical classification of soils according to fertility levels, for humid regions*

MINERAL COMPOSITION	CATION FERTILITY LEVEL
More than 8 per cent heavy feldspars Less than 75 per cent quartz Amphiboles Pyroxenes	Very high
2-8 per cent heavy feldspars Less than 75 per cent quartz Amphiboles Pyroxenes	High
0.5-2 per cent heavy feldspars Less than 75 per cent quartz Amphiboles Pyroxenes	Above medium
Less than 0.5 per cent feldspars Less than 75 per cent quartz Amphiboles Pyroxenes	Medium
Less than 0.5 per cent heavy feldspars Less than 75 per cent quartz	Below medium
Less than 0.5 per cent heavy feldspars 75-85 per cent quartz	Poor
Less than 0.5 per cent heavy feldspars More than 85 per cent quartz	Very poor

That value should be assigned to the minerals of the sands and silts in terms of their plant nutrient contents was suggested by Stienriede (10) in the following grouping according to different specific gravities:

Group I (specific gravity 2.21-2.56) contains mainly potassium feldspars.

Group II (specific gravity 2.62-2.72) contains plagioclase and quartz.

Group III (specific gravity greater than 2.72) contains mica, amphiboles, augite, iron minerals, and others.

Pelisek (9) suggested a similar grouping with different ranges in specific gravities, as follows:

Group I (specific gravity less than 2.60) contains potassium feldspar.

Group II (specific gravity 2.60 to 2.66) contains quartz and sodium plagioclase.

Group III (specific gravity 2.66 to 2.80) contains sodium and calcium plagioclase, andesine to anorthite.

Group IV (specific gravity greater than 2.80) contains mica, magnetite, epidote, amphibole, augite, and others.

In consequence of many investigations of his own as well as those of Pelisek, Novak (8) suggested the following scheme of soil classification, based on the mineralogical composition of the sand separates (2 to 0.02 mm.):

Per cent weatherable materials*	Mineral strength as productivity
0-10	Very poor
10-20	Weak
20-30	Medium
30-40	Strong
More than 40	Very strong

\* Contains the sum of feldspars and the heavy minerals with specific gravities greater than 2.88.

Such a classification probably puts excessive emphasis on the potassium feldspars and insufficient on the calcium feldspars, and attributes undue importance to all the members in the heavy fraction, many of which cannot contribute to the cation fertility of the soil. Nevertheless, in view of the services of acid colloidal clay in making nutrients from the sands and silts available to plants, there is the suggestion that soil classification may well give attention to the mineral contents of the silts and sands.

#### SUMMARY AND CONCLUSIONS

A study was made in which the chemical composition of soybean plants grown on substrates containing sands and silts from various locations and subjected to reaction with electrodyalyzed acid clay was related to the mineralogical and chemical analyses of these soil separates. A summation of the results and of the conclusion drawn follows:

No growth of the soybean plants could be obtained unless some calcium was released from the sands and silts treated with hydrogen clay.

Acid clay action on silt and sand samples from certain locations made calcium, magnesium, and potassium available; samples from other locations provided only calcium and magnesium; other samples supplied only calcium; and still others gave no measurable amounts of any plant nutrients.

There were indications that phosphorus-bearing minerals are rarely found in sands and silts, as measured by the clay-mineral interactions used.

These coarser soil separates may vary widely in calcium and quartz contents.

Heavy feldspars were present in significant amounts in the samples from Iowa, Utah, North Dakota, and Kansas, and were almost absent from samples from Missouri, southern Illinois, and Mississippi.

Soil classification based on the mineralogical composition of sands and silts is suggested as of help in considering soil productivity and soil needs for calcium, magnesium, and potassium treatments.

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# RELATION OF WIND EROSION TO THE WATER-STABLE AND DRY CLOD STRUCTURE OF SOIL<sup>1</sup>

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In previous papers (4, 6) data were presented to show the relationship between wind erosiveness of soils and their dry clod structure. The experimental results indicated that the highly erosive soil grains vary in size approximately between 0.05 and 0.5 mm. in diameter, whereas the difficultly erosive fractions vary between 0.02 and 0.05 mm. and 0.5 and 1 mm. in diameter. Sizes above 1 mm. and below 0.02 mm. were found to be nonerosive or some of them erosive only at an unusually high velocity of the natural wind. On the basis of wind tunnel experiments, mathematical equations were formulated by which the approximate erosiveness of any freshly cultivated and uniformly mixed soil could be calculated from the dry clod structure. The author was in doubt as to whether these equations would apply to soils that have formed a surface crust following a rain.

The purpose of the investigation outlined in this paper was to find, first, the relation between water-stable and dry clod structure of soil and, secondly, whether the dry clod structure, as determined by the dry-sieving method, can be used as an index of wind erosiveness of less recently cultivated soils as well as of freshly cultivated soils.

Kraminsky (12) showed that a soil pulverized by harrowing became more cloddy after wetting and drying in the field than one which was not originally pulverized. Cole (7) found that irrigation increased the cloddiness of a highly pulverized soil to a degree in excess of that which was not initially pulverized. This suggests that the fine particles resulting from the pulverizing action of tillage machinery tend to cement the soil after it has been wetted and dried, the cementation evidently being due to the breakdown of the soil aggregates to smaller particles.

Davydov (8) attributes the stability of the water-stable aggregates to the organomineral gels high in organic content. When the organic content is low the aggregates formed are unstable, and as a result crust formation takes place. Kaspirov (11) further concludes that the main factor in crust formation is the presence in soils of fine particles less than 0.01 mm. in diameter. He asserts that soil crusts are formed on structureless, fine-grained soils regardless of the quantity and quality of humus or of salts in soil solution.

Hopkins (10) points out that soils high in organic matter and lime have been severely affected by wind erosion in Canada and suggests that both these factors

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may be responsible for the development of a fine soil structure which offers little resistance to the force of wind. Caldwell and Ellis (2) found a high correlation between the combined action of clay and alkali-soluble humus and the size of the water-stable aggregates and conclude that humus and clay are responsible for increasing the resistance of some soils to wind erosion. On the other hand, Hardt (9) concludes from his investigations on muck soils in Bavaria that neither the size of the water-stable grains nor the nature and amount of humus has any appreciable effect on wind erosiveness of soils, but that a very marked effect is produced by the lime content, particularly by that in the clay fraction. He found the lime content of a clay fraction of wind-blown soils to be 20 to 50 per cent higher than that of soils resistant to wind erosion.

In considering the causes of soil erosiveness it is essential to distinguish between the structural soil characteristics influencing wind erosion and the physical and chemical factors that affect these characteristics. Factors such as soil texture, lime content, and the amount and nature of the organic matter influence the structure of the soil, but their exact effect on erosiveness can be measured only after the relationship between soil structure and erosiveness has been determined. In this paper data are presented which show in part the relationship between the water-stable and dry clod structure and wind erosiveness of soils.

#### MATERIALS AND METHODS

Composite samples of cultivated soil taken to about 4 inches in depth, were obtained from 30 major soil types from Manitoba, Saskatchewan, and Alberta. In addition, three composite samples of soil were obtained from freshly accumulated wind drifts found next to or within eroded fields. These three samples represented that portion of the soil which had been moved about by the wind and deposited in mounds next to various obstructions. They were almost entirely composed of individual water-stable aggregates and sand grains which in a dry state did not cohere and which, apart from containing some dust particles smaller than the upper limit of silt, had all the physical characteristics of dry dune sand.

To determine their relative erosiveness samples of cultivated soil were exposed in August, 1940, to identical conditions in trays in the field, and their relative erosiveness was measured at 6-month intervals by exposure to a uniform air stream in the laboratory wind tunnel described previously (3). The trays, each 6 feet long, 6 inches wide, and 2 inches high, were made of wood, except the bottoms, which were composed of a 60-mesh screen to allow passage for percolating rain water. Each tray, containing about 20 pounds of soil, was exposed to the weather on level grassland and was covered with coarse screening to prevent any possible erosion by wind. Each spring and fall the soils were conveyed into the laboratory in an undisturbed condition in the trays and tested for erosiveness.

The test of erosiveness consisted of three particular types of exposure in a wind tunnel. First, the soil was subjected to a 17-m.p.h. wind for 3 minutes, then to a 22-m.p.h. wind for an additional 3 minutes, wind velocity being measured at a 12-inch height. Secondly, the soil was exposed to an abrasive stream of fine dune sand falling through a glass tube from above the tunnel chamber and flowing

along the surface of the ground at the rate of 333 gm. per minute. The duration of the exposure was likewise 3 minutes under a 17-m.p.h. wind and 3 minutes more under a 22-m.p.h. wind. The sand was so highly erosive that virtually none of it remained on the surface of the soil, but the exposed soils eroded to a variable degree, depending on their relative susceptibility to abrasion. On some very cloddy and difficultly abraded soils the weight of sand trapped among the irregularities of the surface was greater than that of the soil removed, thus causing a gain in the weight of the exposed soil. The gains in the weight are designated by minus signs in the tables presented. Thirdly, the soil was placed in a small barrel fitted with a tight lid and mounted on a horizontal shaft. The barrel was rotated slowly end over end three times and the soil was placed back in the tray and again exposed to the wind as in the first two tests. The quantity of soil removed under the three tests constituted a measure of erosiveness that is believed to give an approximate measure of erosiveness of the soil under the varying conditions in the field. The experimental data reported herewith indicate the amounts eroded under each of the three sets of conditions.

To determine the effect of the water-stable aggregate structure on the dry clod structure and erosiveness, samples of the soil obtained from freshly accumulated wind drifts were sieved into fractions of three sizes— < 0.42 mm., 0.42 to 0.83 mm., and 0.83 to 2.0 mm.—, and a small portion of the finest fraction was pulverized gently. The two coarsest fractions and a required amount of the pulverized fraction were added to and mixed with different amounts of the fraction passing through the 0.42-mm. sieve. It was found that neither the texture nor the organic matter content varied to any appreciable extent in the different soil fractions used. Pulverizing changed the texture slightly, but the amounts of the pulverized fraction added to the mixture did not in any case exceed 3 per cent of the total weight of the soil. The mixtures, each of which weighed about 20 pounds, and which were in duplicate, were wetted to about the moisture equivalent, thoroughly air-dried, analyzed with respect to their water-stable composition, and, if suitable, were tested for erosiveness by the method already described. The samples so prepared varied only in the quantity of the water-stable aggregates larger than 0.05 mm. in diameter, but the percentage of the water-stable particles smaller than 0.05 mm., the moisture equivalent, and the organic matter remained virtually constant. Samples not conforming with these characteristics were discarded.

In the experiment on the effect of dispersion of the soil to water-stable particles smaller than 0.05 mm., portions of freshly drifted soil were pulverized gently—just sufficiently to crush some aggregates to sizes somewhat below 0.05 mm. in diameter. The pulverized portions were mixed with the unpulverized portions in varying proportions. The addition of slightly pulverized fraction to the original soil lowered the percentage of coarse water-stable crumbs, but such deficiencies were made up by adding the required amounts of this fraction separated from the original soil by sieving. The samples as prepared varied only in the size of the water-stable aggregates and particles smaller than 0.42 mm. in diameter.

The dry clod soil structure, or cloddiness, was determined by the dry-sieving

method described previously (6), and the water-stable structure by the wet-sieving method of Bouyoucos (1), except that the air-dry soil was immersed in water in a partial vacuum of 20 mm. of mercury instead of in an ordinary atmosphere.

#### EXPERIMENTAL RESULTS

##### *Relation of water-stable aggregates, dry clod structure, and wind erosiveness of soils*

The data in table 1 show the effect of the semierosive and nonerosive water-stable aggregates ( $>0.42$  mm.) on the dry clod structure and wind erosiveness of three widely different soils. An increase in the size and the quantity of these water-stable aggregates caused a marked increase in cloddiness and a consequent decrease in erosiveness. Thus, when the quantity of the water-stable aggregates 0.42 to 0.83 mm. in diameter was increased from 0, as in soil 1, to 12.1 per cent, as in soil 2, the amount of eroded soil decreased from 2,607 to 1,056 gm. Doubling the quantity of this fraction, as in soil 3, reduced the amount of eroded soil to 272 gm., and tripling, as in soil 4, to 65 gm. The trends in the effects of this fraction were the same on all of the soils tested, but the actual effect did not appear to be of equal magnitude in every case.

The data in table 1 indicate further that the larger the water-stable aggregates, the greater was the increase in cloddiness and decrease in erosiveness of the soil. A particularly striking feature of the experiment can be observed in soils 12 and 13 where the practically entire replacement of 15.2 per cent of the 0.42- to 0.83-mm. aggregates by only 8.6 per cent of the 0.83- to 2.0-mm. aggregates increased the cloddiness to an appreciable extent and decreased the amount of erosion from 5,055 to 1,959 gm. It is evident that the 15.2 per cent of the smaller aggregates was much less effective in reducing the erosiveness than approximately half that quantity of the larger aggregates. Similar comparisons can be made with other data shown in table 1.

The data in table 2 show that as the quantity of the water-stable particles smaller than 0.05 mm. in diameter increased, there were a corresponding increase in cloddiness and a consequent decrease in erosiveness. The data show that the initial increments of these fine particles reduced the erosiveness very appreciably but that subsequent increments were less and less effective. When the percentage of these particles is expressed in terms of the logarithm of the amount of eroded soil the curve of erosiveness, as shown in figure 1, becomes a straight line, indicating that wind erosiveness is a logarithmic function of the degree of dispersion of the soil in water. As the two small negative erosion values obtained on highly nonerosive samples of clay cannot be expressed in logarithmic values, they could not be included in figure 1. The negative values were relatively small and on that account were believed to have little practical significance.

It will be seen that the erosiveness curves in figure 1 for loam and sandy loam are approximately parallel to each other, suggesting that the relative effect of these fine fractions on erosiveness is relatively the same in the two soils. The curves for these soils indicate that erosiveness varies approximately as  $\text{antilog}(x - 0.1y)$  where  $x$  represents the position at which the logarithmic curve, if pro-

TABLE 1  
*Relation of water-stable aggregates > 0.42 mm., dry clod structure, and wind erosiveness of soils*

SOIL CLASS	SOIL NUMBER	MOI- TURE EQUIVA- LENT	ORGANIC MATTER	WATER-STABLE AGGREGATES						DRY CLOD DISTRIBUTION						AMOUNTS ERODED					
				>2 mm.	2-0.83 mm.	0.83- 0.42 mm.	0.42- 0.25 mm.	0.25- 0.05 mm.	0.05- 0.02 mm.	<0.02 mm.	>38 mm.	38- 12.7 mm.	12.7- 6.4 mm.	6.4- 2.0 mm.	2.0- 0.83 mm.	0.83- 0.42 mm.	<0.42 mm.	Con- dition 1*	Con- dition 2†	Con- dition 3‡	Total
				per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	gm.	gm.	gm.	gm.
Clay	1	38.2	2.09	0	0	0	29.2	52.8	13.5	4.5	0	3.0	3.0	1.1	0.2	3.2	89.5	97	1013	1497	2607
	2	37.9	2.11	0	0	12.1	31.0	39.4	12.9	4.6	0	1.5	3.7	4.2	4.2	22.9	63.5	22	441	593	1056
	3	38.4	2.09	0	0.7	23.4	31.6	26.7	13.1	4.5	0	3.2	3.0	7.2	10.5	19.2	56.9	20	149	103	272
	4	37.5	2.10	0	1.3	36.6	23.9	20.0	13.7	4.5	0	11.9	5.4	13.2	19.7	29.7	20.1	10	43	12	65
	5	36.1	2.12	0	25.6	28.4	16.3	11.9	13.2	4.6	5.4	6.0	1.6	6.6	58.5	11.9	10.0	Tr.	-15	Tr.	-15
Loam	6	21.0	1.11	0	0	0.7	18.3	61.7	15.2	4.1	0	2.0	11.6	3.2	3.9	13.2	66.1	20	248	367	635
	7	20.3	1.13	0	1.0	16.5	25.8	37.4	14.7	4.6	0	2.9	9.8	4.1	5.1	21.0	57.1	13	197	278	488
	8	20.5	1.11	0	2.1	31.3	20.5	27.4	14.6	4.0	0	6.0	10.8	3.9	4.1	27.0	48.2	8	180	192	380
	9	19.7	1.12	0	7.3	37.8	17.6	17.7	15.2	4.4	0	2.7	9.1	7.9	15.4	21.8	43.1	5	51	27	83
	10	9.7	1.10	0	0	0	3.9	89.6	5.5	1.0	0	0	0	0	0.3	1.6	98.1	2290	2097	2309	6696
Fine sandy loam	11	8.9	1.10	0	0	8.5	4.9	80.6	5.0	1.0	0	0	0	0	0.8	12.5	86.7	2289	2103	2195	6587
	12	8.1	1.10	0	0	15.2	5.7	73.0	5.0	1.1	0	0	0	0	0.4	20.5	79.1	1755	1248	2052	5055
	13	8.8	1.09	0	8.6	1.5	3.5	80.2	5.2	1.0	0	0	4.0	0	6.9	17.6	71.5	283	893	783	1959
	14	7.7	1.09	0	6.2	14.6	5.4	68.2	4.5	1.1	0	0	3.9	0.2	10.4	2.0	83.5	123	806	521	1450

\* Exposure to wind only.

† Exposure to sand abrasion and wind.

‡ Rotation in barrel before exposure to wind.

TABLE 2  
*Relation of water-stable particles < 0.05 mm. in diameter, dry clod structure, and wind erosiveness of different soils*

SOIL CLASS	SOIL NUMBER	MOISTURE EQUIVALENT	ORGANIC WATER	WATER-STABLE AGGREGATES								DRY CLOD DISTRIBUTION								AMOUNTS ERODED			
				>2 mm.	2-0.83 mm.	0.83-0.42 mm.	0.42-0.25 mm.	0.25-0.05 mm.	0.05-0.02 mm.	<0.02 mm.	>38 mm.	38-12.7 mm.	12.7-6.4 mm.	6.4-2.0 mm.	2.0-0.83 mm.	0.83-0.42 mm.	<0.42 mm.	Con-dition 1*	Con-dition 2†	Con-dition 3‡	Total		
			per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	gm.	gm.	gm.	gm.				
Clay	15	40.1	2.50	0	1.2	21.4	28.1	31.7	10.0	7.6	0	0	1.3	4.9	6.0	35.8	51.4	13	127	1045	1185		
	16	37.0	2.48	0	1.3	21.3	23.4	28.3	14.1	11.6	2.3	23.4	17.8	14.0	3.8	19.8	18.9	9	49	211	269		
	17	39.6	2.48	0	1.3	17.7	19.8	29.4	17.0	14.8	0	48.0	24.4	10.5	2.5	6.8	7.8	0	-35	0	-35		
	18	38.0	2.50	0	0.8	19.8	19.0	21.2	20.5	18.7	24.3	39.9	25.5	6.5	0.6	0.7	2.5	0	-101	0	-101		
Loam	19	21.0	1.73	0	0	3.1	5.7	77.8	11.5	1.9	0	0	0	0.5	0.9	22.8	75.8	278	2507§	3216§	6001		
	20	21.2	1.74	0	0	2.8	4.3	70.5	14.8	7.1	0	0	0	0.8	6.9	16.7	75.6	2	787	1759	2539		
	21	21.4	1.73	0	0	3.7	2.8	63.7	16.9	12.9	0	25.1	7.7	5.2	1.6	6.0	54.4	0	267	428	695		
	22	21.5	1.74	0	0	3.9	2.5	54.5	21.4	17.7	2.3	40.2	7.4	6.1	4.5	1.4	38.1	0	159	70	229		
Fine sandy loam	23	8.2	1.23	0	0	1.2	4.4	86.4	4.0	0	0	0	0	0	0	1.0	99.0	2304§	3894§	3640§	9838		
	24	9.9	1.25	0	0	1.4	2.1	82.4	9.1	5.0	0	10.6	2.2	5.9	1.9	1.6	77.8	59	1416	1755	3230		
	25	12.1	1.25	0	0	0.9	1.3	72.8	13.9	11.1	2.5	16.1	6.1	6.6	1.7	7.1	59.9	9	548	295	852		
	26	14.5	1.27	0	0	1.0	0.5	63.8	19.1	15.6	11.3	27.0	7.3	7.5	2.2	1.2	43.2	0	243	112	355		

\* Exposure to wind only.

† Exposure to sand abrasion and wind.

‡ Rotation in barrel before exposures to wind.

§ Continuously uniform soil flow.

jected, will meet the ordinate, and  $y$  the percentage of the water-stable particles  $<0.02$  mm. The value of the constant 0.1 will vary with the method used in determining the percentage of the water-stable particles, and probably also with the nature of the soil. The value of  $x$  is not the same for all soils and is apparently dependent on the relative effect of other factors on the erosiveness of the soil.

Soil 23 in table 2, which contained no water-stable fractions smaller than 0.02 mm. in diameter, remained in a single-grain structure after it was thoroughly wetted, dried, and stirred, but other soils that contained fractions smaller than 0.02 mm. aggregated to some extent, the degree of aggregation varying directly with the quantity of these fine particles. When a tray containing this soil was tilted at 45 degrees from the horizontal, the soil did not flow, as it did before

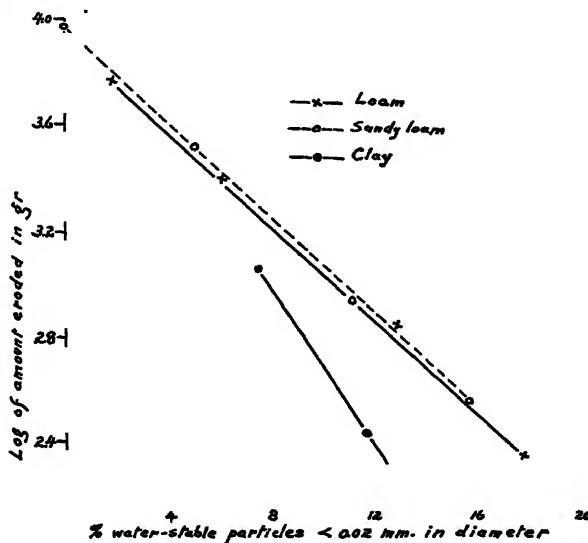


FIG. 1. RELATIONSHIP BETWEEN WIND EROSION AND PERCENTAGE OF WATER-STABLE PARTICLES  $<0.02$  MM. IN DIAMETER

wetting, but remained as a rigid body, indicating that there was a slight cohesion between the particles. The surface of this soil contained some loose sand grains which under a wind force produced sufficient abrasion to maintain a uniform rate of erosion, the nature and the intensity of erosion differing little from that of ordinary dune sand. It is evident that the water-stable fractions 0.02 to 0.05 mm. in diameter were much less effective in increasing the cloddiness and decreasing the erosiveness than fractions smaller than 0.02 mm. in diameter.

#### *Relation between the dry clod structure and computed and determined erosiveness*

Representative data in table 3 show the water-stable aggregate structure, the dry clod structure, the computed erosiveness and the determined erosiveness of some major soil types from the provinces of Manitoba, Saskatchewan, and Alberta. The soils in table 3 are arranged in order of their average erosiveness

TABLE 3  
Structural characteristics of soils from different regions and their computed and determined erosiveness

SOIL TYPE OR CLASS	DATE	WATER-STABLE AGGREGATES										DRY CLOUD DISTRIBUTION										COMPUTED EROSIVENESS*	AMOUNTS ERODED										
		>2 mm.		2-0.83 mm.		0.83-0.42 mm.		0.42-0.25 mm.		0.25-0.05 mm.		<0.02 mm.		>38 mm.		38-12.7 mm.		12.7-6.4 mm.		6.4-2.0 mm.			2.0-0.83 mm.		0.83-0.42 mm.		<0.42 mm.		Con- dition 1"	Con- dition 2"	Con- dition 3"	Total	
		per cent	gm.	per cent	gm.	per cent	gm.	per cent	gm.	per cent	gm.	per cent	gm.	per cent	gm.	per cent	gm.	per cent	gm.	per cent	gm.		per cent	gm.	per cent	gm.	per cent	gm.					
Almæssipi fine sandy loam	May '41	0.9	1.8	3.6	5.4	72.2	8.0	8.1	0	1.0	1.4	3.9	3.6	5.9	84.2	4.67	86	165	713	964	86	165	713	964	4.67	86	165	713	964	86	165	713	964
	Oct. '41	0	1.0	5.8	8.8	70.4	10.0	4.0	0	1.0	2.7	4.9	3.6	5.1	82.7	4.19	25	139	865	529	25	139	865	529	4.19	25	139	865	529	25	139	865	529
	May '42	0	0.9	4.1	4.9	73.8	11.1	5.2	0	0	0.4	2.7	2.8	5.7	88.9	5.70	88	874	1228	2190	88	874	1228	2190	5.70	88	874	1228	2190	88	874	1228	2190
	Average	0.8	1.2	4.5	6.4	72.1	9.7	5.8	0	0.7	1.5	3.8	3.5	5.6	84.9	4.85	66	318	769	1228	66	318	769	1228	4.85	66	318	769	1228	66	318	769	1228
Regina heavy clay	May '41	0.8	2.9	19.2	28.1	27.4	8.0	13.6	0	0.8	5.1	6.8	7.1	27.9	52.3	1.42	32	90	126	248	32	90	126	248	1.42	32	90	126	248	32	90	126	248
	Oct. '41	0.2	1.1	14.2	32.7	31.3	13.0	7.5	0	1.2	3.2	5.9	8.7	35.9	45.1	1.16	16	103	71	190	16	103	71	190	1.16	16	103	71	190	16	103	71	190
	May '42	0.5	1.2	15.3	29.7	32.9	10.1	10.3	0	0	1.2	2.2	2.3	30.9	63.4	4.95	134	1010	969	2113	134	1010	969	2113	4.95	134	1010	969	2113	134	1010	969	2113
	Average	0.5	1.7	16.2	30.2	30.5	10.4	10.5	0	0.7	3.2	5.0	6.0	31.6	53.5	2.51	61	401	389	850	61	401	389	850	2.51	61	401	389	850	61	401	389	850
Hatton fine sandy loam	May '41	1.7	2.0	7.4	26.5	41.9	11.5	9.0	0	6.1	2.7	5.0	5.7	8.2	72.3	2.62	44	61	287	392	44	61	287	392	2.62	44	61	287	392	44	61	287	392
	Oct. '41	0.6	1.2	11.7	23.7	42.1	12.0	8.7	0	8.1	4.8	5.7	4.2	8.2	69.0	2.30	26	84	202	312	26	84	202	312	2.30	26	84	202	312	26	84	202	312
	May '42	0.9	1.8	9.7	22.3	45.0	12.2	8.1	0	1.8	1.9	3.5	3.4	10.6	78.8	4.97	109	874	742	1725	109	874	742	1725	4.97	109	874	742	1725	109	874	742	1725
	Average	1.1	1.7	9.6	24.1	43.0	11.9	8.6	0	5.3	3.1	4.7	4.4	9.0	73.5	3.30	60	340	410	810	60	340	410	810	3.30	60	340	410	810	60	340	410	810
Fine sandy loam (Clareholm, Alta.)	May '41	6.4	2.0	5.3	11.3	50.4	11.0	13.6	0	7.9	4.2	8.4	9.1	9.5	60.9	0.89	44	88	84	166	44	88	84	166	0.89	44	88	84	166	44	88	84	166
	Oct. '41	2.4	2.3	7.9	14.1	49.1	16.5	7.7	0	8.2	8.5	8.5	5.6	7.8	61.4	1.06	20	83	74	177	20	83	74	177	1.06	20	83	74	177	20	83	74	177
	May '42	1.7	3.1	4.4	10.9	58.7	13.3	7.9	0	8.4	3.5	6.2	5.2	11.5	65.2	1.95	66	550	245	861	66	550	245	861	1.95	66	550	245	861	66	550	245	861
	Average	3.5	2.5	5.9	12.1	52.7	13.6	9.7	0	8.2	5.4	7.7	6.6	9.6	62.5	1.30	43	224	134	401	43	224	134	401	1.30	43	224	134	401	43	224	134	401
Waskada clay loam	May '41	5.7	4.7	10.7	13.0	30.3	20.0	15.6	1.0	6.3	4.9	7.1	8.2	11.2	61.3	0.98	25	70	106	201	25	70	106	201	0.98	25	70	106	201	25	70	106	201
	Oct. '41	0	0.6	6.6	15.0	39.8	26.0	12.0	5.1	5.7	4.3	7.2	7.3	11.7	58.7	1.09	15	90	61	166	15	90	61	166	1.09	15	90	61	166	15	90	61	166
	May '42	3.4	3.9	8.3	13.1	37.5	22.5	11.3	0	8.3	3.7	6.7	8.1	11.7	66.4	1.52	42	152	292	486	42	152	292	486	1.52	42	152	292	486	42	152	292	486
	Average	3.0	3.1	8.5	13.7	35.9	22.8	13.0	2.0	5.1	4.3	7.0	7.9	11.5	62.2	1.20	27	104	153	284	27	104	153	284	1.20	27	104	153	284	27	104	153	284
Oxbow loam	May '41	4.2	4.1	11.1	15.3	30.7	17.0	17.6	0	6.0	4.1	10.1	7.9	12.0	59.9	0.93	34	330	67	131	34	330	67	131	0.93	34	330	67	131	34	330	67	131
	Oct. '41	0.8	1.0	14.4	20.8	29.8	19.0	14.2	0	14.4	10.7	6.8	6.6	12.7	48.8	0.51	26	21	50	97	26	21	50	97	0.51	26	21	50	97	26	21	50	97
	May '42	3.1	2.8	11.8	21.1	28.7	18.9	13.6	0	3.0	9.0	4.7	5.3	13.0	65.0	1.55	40	153	330	523	40	153	330	523	1.55	40	153	330	523	40	153	330	523
	Average	2.7	2.6	12.4	19.1	29.8	18.3	15.1	0	7.8	7.9	7.2	6.6	12.6	57.9	1.00	33	68	149	250	33	68	149	250	1.00	33	68	149	250	33	68	149	250

Red River clay	May '41	7.4	10.5	19.8	16.9	18.1	11.0	16.3	0	0	9.0	11.2	15.2	20.5	44.1	0.29	14	55	25	94
	Oct. '41	0	2.6	19.8	29.0	23.0	14.0	11.6	0	8.7	10.3	13.7	29.7	24.3	13.3	0.02	19	-89	Tr.	-70
	May '42	0	1.9	16.7	28.8	30.7	10.9	11.0	0	0	0.5	1.4	8.7	41.1	48.3	2.20	59	141	472	672
	Average	2.5	5.0	18.8	24.9	23.8	12.0	13.0	0	2.9	6.6	8.8	17.9	28.6	35.2	0.84	31	36	166	232
Haverhill loam	May '41	3.5	4.5	12.4	12.3	35.1	18.5	13.7	3.9	7.3	5.9	6.8	9.0	11.7	55.4	0.73	31	26	62	119
	Oct. '41	2.6	2.5	12.9	15.0	31.0	27.0	9.0	9.1	11.4	7.4	8.0	7.1	12.1	44.9	0.35	14	35	20	69
	May '42	2.3	3.2	11.1	16.0	31.0	24.1	12.3	3.0	9.3	4.5	6.4	6.4	15.8	54.6	1.09	37	38	133	213
	Average	2.8	3.4	12.1	14.4	32.4	23.2	11.7	5.3	9.3	5.9	7.1	7.5	13.2	51.7	0.72	27	33	73	143
Loam (Sibbald, Alta.)	May '41	10.5	4.2	8.3	14.8	36.8	13.5	11.9	3.8	8.1	3.8	7.1	9.7	13.6	53.9	0.71	26	42	60	128
	Oct. '41	11.0	3.4	7.8	16.7	37.1	16.5	7.5	3.0	14.6	8.2	11.2	8.9	13.2	40.9	0.22	18	-18	25	25
	May '42	7.1	1.8	8.0	16.1	40.6	14.3	12.1	4.5	12.8	5.5	6.8	7.0	14.5	48.9	0.60	13	64	64	141
	Average	9.5	3.1	8.0	15.9	38.2	14.8	10.5	3.8	11.8	5.8	8.4	8.5	13.8	47.9	0.51	19	29	50	98
Saline clay (Val Marie, Sask.)	May '41	10.7	13.0	16.4	12.7	16.7	9.5	21.0	0	2.3	5.9	10.1	17.7	34.1	29.9	0.24	14	32	22	68
	Oct. '41	0.4	6.0	21.2	18.6	26.6	11.0	16.2	0	15.5	17.0	23.8	23.3	12.3	8.1	Tr.	Tr.	-81	Tr.	-81
	May '42	6.3	10.9	14.8	17.8	20.0	12.3	17.9	0	0.3	1.2	2.5	22.0	35.0	39.0	0.50	17	-67	157	107
	Average	5.8	10.0	17.5	16.4	21.0	10.9	18.4	0	6.0	8.0	12.1	21.0	27.1	25.8	0.25	10	-39	60	31

\* Computed from the dry clod distribution according to the formula:

$$q = \text{antilog} \left[ \frac{0.75C + 1.14D + 1.49E + 1.80F}{C + D + E + F} - 0.6 \frac{D + E + F}{C + D + E + F} \times \frac{B}{A + B} - 0.042 (C + D + E + F) \right]$$

where  $q$  = amount erodible soil in kilograms/square meter,

$A$  = per cent clods < 0.42 mm. in diameter

$B$  = per cent clods 0.42- 0.83 mm. in diameter

$C$  = per cent clods 0.83- 2.0 mm. in diameter

$D$  = per cent clods 2.0 - 6.4 mm. in diameter

$E$  = per cent clods 6.4 -12.7 mm. in diameter

$F$  = per cent clods > 12.7 mm. in diameter

† Exposure to wind only.

‡ Exposure to sand abrasion and wind.

§ Rotation in barrel before exposure to wind.



determined by wind tunnel tests. On the whole, the sandy soils and some clays were more erosive than the medium-textured soils, the former evidently on account of the lack of cementing materials necessary to bind the individual grains together, and the latter because the clods could not withstand the disintegrating influence of the weather, thus readily breaking down to a finely granulated, erosive condition. The most highly erosive fine sandy soil possessed an extremely low percentage of the wind-resistant water-stable aggregates greater than 0.42 mm. in diameter and a very low percentage of the fine cementing fractions smaller than 0.02 mm. As may be expected, such soils possess a very poorly developed clod structure and are extremely susceptible to erosion by wind.

The water-stable aggregate structure of many soils did not differ very greatly, yet the dry clod structure and erosiveness varied very markedly. It is evident that the water-stable aggregate structure is not the only physical characteristic affecting the dry clod structure and wind erosiveness of soils but that other factors not determined in this investigation are likewise responsible to a considerable extent.

A comparison of the quantities of soil eroded in a wind tunnel with those computed from the dry clod structure according to the formula given under table 3 shows that there is a fairly good agreement between the order of the two. The actual differences between the computed and the determined erosiveness are due to the fact that the computed erosiveness designates the total quantity of soil removable from a freshly cultivated soil by wind ranging from 17 to 22 m.p.h. at 1-foot height, whereas the determined erosiveness designates the amounts eroded during a definite interval of time under different conditions of soil and wind. The quantity of eroded soil does not represent the total removable amount but merely indicates the relative intensity of erosion for the period of exposure. When, however, the roughness of the soil surface is the same, the relative intensity and the total quantity of erodible soil vary directly with each other (5), and consequently one or the other could serve as a measure of erosiveness. The computed erosiveness was based on the general formula based on wind tunnel experiments that have been described previously (4, 6).

On the whole, the soils that were highly erosive before cultivation (condition 1, table 3) were also highly erosive after (condition 3), whereas those registering low erosiveness before cultivation also registered low erosiveness after. The amounts of soil eroded under these two conditions and under sand abrasion (condition 2) varied directly with computed erosiveness. The regression of the amount of eroded soil on computed erosiveness was estimated by the method of least squares. The regression coefficient for conditions 1, 2, and 3, and for the total amount of eroded soil, was found to be 16.0, 128.8, 175.1, and 324.2, and the significance of regression, usually designated by  $t$ , was found to be 8.33, 6.18, 14.07, and 11.06, respectively. The regression in all these cases is far above the high level of significance, which in this instance is 2.76. It is evident that the computed erosiveness based on the dry clod structure of soils is a reliable index of the actual erosiveness of less recently cultivated soils (condition 1 and 2) as well as of freshly cultivated soils (condition 3).

The data indicate that the water-stable aggregate structure and the dry clod structure did not remain the same throughout the period of exposure to the weather but changed to some extent, the amount of change varying markedly in different soils. On the whole, the water-stable aggregate structure was subject to considerably smaller variation than the dry clod structure, but it did change appreciably in many soils. In most soils the percentage of the non-erosive clods was higher and the percentage of erosive fractions lower at the beginning of the exposure period than at the end. The disintegration of clods occurring within that period was evidently due to the effects of continuous fallowing. The relative erosiveness of all soils varied directly with their dry clod structure.

The data in table 3 indicate further that all soils were more cloddy in October, 1941, than in the preceding or succeeding May, the computed and determined erosiveness being proportionately lower in October. The seasons of the year undoubtedly have a marked influence on the dry clod structure and consequently on wind erosiveness of soils, but as shown by the data they have practically no effect on the water-stable structure. For this reason the water-stable structure might be regarded as the only true indicator of the physical nature of the soil. On the other hand, it is evident that it cannot be regarded as a single criterion influencing wind erosiveness. The erosion of the soil in the Prairie Provinces of Canada occurs mainly during the months of April and May, but the increased erosion during that period can be attributed not only to the increased erosiveness of the soil, but likewise to the increase in the velocity of wind and other factors.

#### DISCUSSION AND CONCLUSIONS

It is evident from this investigation that wind erosiveness is determined not so much by the size of the ultimate mechanical fractions, as by the size of the individual aggregates or clods that enter into the composition of the soil. The results of experiments showed that the dry clod structure, as determined by dry-sieving, can be used as an approximate index of wind erosiveness of freshly cultivated and less recently cultivated soils.

An increase in the size or quantity of coarse water-stable aggregates ( $>0.42$  mm.) was found to increase the cloddiness and decrease the erosiveness of a soil. An increase in the quantity of the water-stable particles smaller than  $0.05$  mm., and particularly of those smaller than  $0.02$  mm., likewise increased the cloddiness of the soil and decreased its erosiveness. Since many soils of a similar water-stable structure varied widely with respect to erosiveness, it is evident that other factors must also play an important role in determining the clod structure and erosiveness of the soil. A change in the water-stable structure cannot be regarded as an indication of a change in wind erosiveness unless it is certain that other factors that might effect erosiveness remain the same.

The relatively high resistance to erosion of Red River clay and some other soils (table 3) seems to be due partially to the large size of the water-stable aggregates. On the other hand, Regina heavy clay and other similar lacustrine clay soils are highly erosive, partly because the size of the water-stable aggregates is

generally too small to resist the action of the wind. The high state of aggregation of a soil is apparently not so important as the size of the water-stable granules. Aggregation may, or may not, increase the resistance of the soil to wind erosion, the deciding factor being whether the granules or clods are sufficiently large to withstand the erosive force of wind. On the other hand, the high resistance of saline clay from Val Marie, Saskatchewan, is apparently predominantly due to both the large size of many water-stable granules and the high dispersion on wetting to small particles and consequent cementation into massive clods when the soil is dried. The most erosive soils were found to contain relatively large quantities of the intermediate water-stable aggregates of the size ranging approximately between 0.02 and 0.5 mm., and particularly between 0.05 and 0.25 mm. in diameter.

The computed erosiveness, as determined for the soils studied, agreed, on the whole, fairly closely with the order of erosiveness as determined by wind tunnel tests. The formula employed in the computation takes into account only the dry clod soil structure, which is affected by a number of factors, the nature and the relative influence of most of which are not at present thoroughly understood.

#### SUMMARY

A close relation was found between wind erosiveness and the water-stable and dry clod structure of different soils. The computed erosiveness, based on the dry-sieving analysis of the soil, varied approximately with the actual erosiveness determined by wind tunnel tests. It was concluded that the dry clod structure, as determined by dry-sieving, can be used as an approximate index of wind erosiveness of less recently cultivated soils that have formed a surface crust following a rain, as well as of freshly cultivated soils.

An increase in the quantity of coarse water-stable aggregates ( $>0.42$  mm.) increased the cloddiness and consequently decreased the erosiveness of the soil. An increase in the quantity of fine water-stable particles ( $<0.02$  mm.) produced the same effects. Many soils possessing a similar water-stable aggregate structure varied appreciably in cloddiness and erosiveness, suggesting that other factors besides the water-stable aggregate structure might influence the dry clod structure and erosiveness of soils.

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# FORMATION OF WATER-STABLE STRUCTURE IN PUDDLED SOILS<sup>1</sup>

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Although little is yet known about the exact mechanics of soil structure formation, it is believed that the mechanical actions accompanying wetting and drying, shrinking and swelling, freezing and thawing, and the growth of plant roots cause the rearrangement of soil particles into structural groups. It has also been observed that certain materials in the soil such as some of the cations, principally calcium and hydrogen, iron hydroxides, and organic matter are associated with the occurrence of those structures in which a high percentage of the aggregates are water-stable. Although many of these relationships are taken for granted, their exact functional values have seldom been worked out, largely because of the inherent difficulties in describing soil structural properties in precise and quantitative terms. There is a need for clarification of the concept of soil structure and for the development of objective and quantitative measurements of the natural physical state of field soils (3).

## HISTORICAL REVIEW

### *Evaluating soil structure*

Because the soil is such a commonplace thing, the words describing it are common words with many shades of meaning varying with time and locality. Although attempts have been made to assign limited meanings to common soil terms for the sake of precise and accurate description, some of the confusion still persists.

The Anglo-Saxon "tilth" has come to mean (31) "the physical condition of a soil in respect to its fitness for the growth of a specified plant." But the word "structure" as commonly used still possesses ambiguity. Some use "structure" synonymously with "aggregation." In the glossary of the 1938 Yearbook of Agriculture (31), "structure" is defined as follows: "the morphological aggregates in which the individual soil particles are arranged." If this limited definition is accepted, there seems to be a need for some word to describe that condition of the soil which is neither structure nor tilth by the foregoing definitions but which lies in the realm between. It is that whole morphological condition of the soil which results from the arrangement of the soil mass, whether it be beneficial or harmful to plants, and which is an intrinsic quality of the soil itself, regardless of the nature of the vegetation upon it.

Baver (2), Weir (33), Kolodny and Neal (11), and Lyon and Buckman (13) refer to soil structure as "the arrangement of soil particles," a definition which would seem to have broader implications than that structure is merely the aggregates themselves. Nikiforoff (18) defines structure as a condition of the soil in which the primary particles like sand, silt, and clay are arranged into various aggregates. To some a picture of soil structure is not complete unless it is descriptive of the pore space as well as the solid material. Others

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(12, 23) think of the natural soil structure as the complete pattern of pore space and solid material as it occurs naturally in the soil in undisturbed condition. To these persons, aggregation, although it contributes markedly to structure, is not synonymous with it.

Regardless of definition, aggregation is obviously so closely related to all the different concepts of soil structure that measurements of the soil aggregates must be closely related to the structure of any given soil. Difficulties are met, however, in finding accurate means of describing and characterizing even so definite a property as aggregation. Morphological characteristics of individual aggregates that can be isolated from the soil and that show up best when the soil is nearly air-dry, have proved useful to soil classification (18).

"Good structure" as commonly used in reference to surface soils, usually means either a granular or a water-stable structure or both. The methods proposed for the evaluation of the structure of wet soils consist for the most part of means of determining the size distribution of the water-stable aggregates. Although the methods are arbitrary, they are valuable because they furnish quantitative information about soil aggregation which can be obtained quickly and objectively. The wet-sieve method as described by Yoder (34) is frequently used. Such methods do not portray a complete picture of the natural state of the soil. A better idea of the complete pattern of solid and pore space can be attained with such tension methods as that described by Russell (25). Because of its accuracy and simplicity Kolodny and Neal (11) recommended a dispersion method for measuring aggregation. Their results were expressed as the percentage of the total mechanical separates less than  $40\mu$  that were "microaggregated" in particles greater than  $40\mu$ . In the study reported in this paper, aggregate analysis was selected as the means for measuring water-stable structure, and a microscopic method (22) was chosen because it was adapted to the study of small samples and because it made possible direct observation of the morphological characteristics of the aggregates.

#### *Effect of organic matter and microbiological activity on development of water-stable aggregates in soil*

Many observations have been made of the beneficial effect of organic matter on soil structure (1, 4, 5, 6, 7, 8, 16, 24). Studies of this effect have led naturally to investigations of the microbiological processes responsible for the chemical and physical changes in organic materials upon their return to the soil. The exact nature of the changes and their influence on structure have not been worked out. It is generally thought (20), however, that the effects of organic matter on structure may be due to the binding action of the decomposition products of plant residues, to mechanical binding by microbiological growth structures such as fungal mycelia or masses of bacterial cells, and to the cementing action of secretory products of microorganisms such as mucus, slime, or gum.

Chemical changes resulting from microbial activity doubtless affect the nature of the materials that hold the discrete particles in clumps. Myers (17) assumed that colloidal organic matter and inorganic colloids united chemically and thought that the stability of aggregates bound by organic colloidal material was due to the irreversibility of such colloids following dehydration. Sideri (29) believed aggregates resulted from the establishment of a firm bond between clay and quartz sand, the nature of the aggregates depending on the colloidal part (28). Furthermore, he (29) claimed that a clay-humus bond developed as a result of mutual orientation based on similar crystalline periods. Where an excess (30) of humus occurred in a sand-clay-humus mixture, the mass, on drying or freezing, would separate out into two parts, one containing an anisotropic combination of sand, clay, and humus, and the other, organic matter. This latter material, because it had a higher surface tension than the anisotropic center, would separate from the mixture after the clay was "saturated" with humus and distribute itself at the periphery of the anisotropic central mass, producing the typically spherical shapes of granular aggregates.

It is difficult to separate the granulating influence of organic compounds in the soil from the influence of calcium, hydrogen, iron hydroxide, and other materials known to be associated with aggregation. In some cases the granulation may possibly result from some

combination of such materials. Martin and Waksman (15) noted that the effect of lime on aggregation seemed to be associated with its effect upon the action of the organic binding material, an observation in line with the ideas of Kubiřna (12) and of Bradfield and Jamison (3), who suggested that soil structure formation depended more on cementation processes than on the flocculating effect of calcium. The role of lime on granulation may lie in its effect in creating a medium favorable to the production of sticky materials in the decomposition of organic matter. Shrikhande (26) found a neutral reaction essential to the production of stickiness in manure heaps.

Soil treated with organic matter and incubated at favorable moisture and temperature conditions will be bound into rather stable masses by intricate, interlacing networks of fungal mycelia. This phenomenon can be readily observed and has been described by Waksman and Martin (32). There is some speculation that soils may be bound into aggregates by masses of bacterial cells.

It was noted that certain organic materials such as celluloses and oat straw would yield sticky mucilages (9, 10, 26, 27). This suggested the possibility of such materials acting as binding substances for soil aggregates (21), a possibility which was successfully explored by Kanivetz and Korneeva (10), Martin and Waksman (15), Peele (20), and Peele and Beale (21).

Peele (20) found that pure mucus produced by bacteria could effectively bind soil into water-stable aggregates, provided the soil and mucus were kneaded together into granules and air-dried. The binding action was attributed to the natural cohesion of the mucus for soil and to the irreversibility of the mucus on dehydration. Additions of sucrose to Cecil sandy loam and inoculation with microorganisms resulted in an increased number of large water-stable aggregates upon incubation. When added under aseptic conditions, the fungi were more effective than bacteria.

The natural assumption has been that anything which increased the number of large water-stable aggregates would increase infiltration and decrease runoff. Peele and Beale (21) tested this theory in field plots where they checked the actual effect on erosion of the aggregation resulting from additions of organic matter and microbiological cultures to soil. Sucrose plus inoculation with *Penicillium oxalicum* produced both an increase in aggregation and a decrease in runoff and erosion.

#### EXPERIMENTAL

This experiment was planned to test the effect of the products of decomposition of certain organic materials on the capacity of soil to assume a highly aggregated, water-stable structure. The basic procedure was to mix organic matter with the soil, incubate it for a month, puddle the mixture thoroughly, and then induce the development of aggregation by exposing the soil to wetting and drying.

Soil from the B horizon of Tama silt loam from near Gladbrook, Iowa, was selected for use throughout the experiment because the scarcity of large primary particles in this loessial material would simplify the study of aggregation. The mechanical analysis by the method of Olmstead *et al.* (19) and the numbers of discrete grains per gram by direct count (22) are presented in table 1.

The organic materials were added in triplicate to the soil samples at a rate equivalent to 5 tons per acre (2,000,000 pounds). The pattern of the experiment was three 100-gm. samples of untreated soil, three samples of soil plus ground alfalfa, three of soil plus ground cornstalks, and three of soil plus sucrose. The samples were incubated for 30 days at 30°C. and at 50 per cent saturation capacity. As a check on the influence of microbiological activity on the effects resulting from additions of organic matter, another similar set was mixed and sterilized in a steam autoclave at 15 pounds' pressure for 15 minutes on each of



three consecutive days and incubated under aseptic conditions. In order to amplify the possible effects of the ordinary rate of application a third set was run similar to the unsterile set except that the rate of application was increased to 50 tons per acre.

*Test for uniformity of aggregate formation following puddling*

In order to check the uniformity of structure developing in similarly puddled and treated samples, the soil was puddled and allowed to wet and dry 10 times. The samples were puddled by manipulation when at a moisture content close to the moisture equivalent as described by McGeorge (14). At first the samples were molded in the bottoms of beakers, but it was impossible to avoid folds and cracks. It was found that the most uniform physical condition could be obtained by working the soil into small marbles about 1 cm. in diameter. The balls were wetted in the spray of a power atomizer and placed in an evacuated desiccator

TABLE 1  
*Primary particles in a sample of the B horizon Tama silt loam*

SEPARATE	PERCENTAGE OF TOTAL WEIGHT	NUMBER PER GRAM
Medium sand.....	0.2	0
Fine sand.....	0.2	0
Very fine sand.....	3.6	673,000
Silt.....	57.7	460,000,000
Clay 0.005 to 0.002 mm.....	5.1	
Clay 0.002 to 0.001 mm.....	4.6	
Clay less than 0.001 mm.....	28.5	
Total.....	99.9	

for 2 hours to aid the capillary distribution of the moisture. After each wetting the samples were air-dried at room temperature. After the final drying the balls were slaked for 1 hour in water. Then the clear water was syphoned off, the sample was dispersed in glycerine, and three plates were poured for counting (22). The averages of the three counts per ball are shown in the upper part of table 2.

The uniformity of aggregation was better than was expected. Since most sand grains could be distinguished, they were counted to give an idea of the proportional sand content. Enough sand grains were insufficiently distinguishable from aggregates, however, to subject this mode of separation to some error, as shown by the variability between sand and aggregates of a given size as compared with the total counts of sand plus aggregates in the same size class. Nevertheless, the number of sand grains in each size group was fairly well indicated.

The natural drying of the samples closely resembled field conditions, but because of the time involved, a test was made of the uniformity of aggregation occurring where the samples were dried on a tray 10 inches above a large hot plate kept at 60°C.

The values given in the lower part of table 2 show that the uniformity was not lessened by this treatment but that the artificial heating resulted in better aggregation in all the sizes counted. Because of the saving in time, this treatment was used in the rest of the experiment, on the assumption that the aggregation, although better than would occur at low drying temperatures, would still reflect differences in treatment in the order of their expected effects under natural conditions.

TABLE 2  
*Test of uniformity of aggregation in puddled soil*  
Counts in thousands per gram

PUDDLED BALLS BY NUMBER	>0.5 MM. AGGREGATES	>0.25 MM. AGGREGATES	0.25-0.1 MM. AGGREGATES	0.1-0.05 MM.			0.05-0.02 MM.		
				Aggregates	Sand grains	Total	Aggregates	Sand grains	Total
<i>Puddled soil wetted and dried at room temperature*</i>									
1		8	76	640	400	1,040	546	960	1,506
2		11	65	556	266	822	360	1,030	1,390
3		8	63	517	280	797	387	998	1,385
4		7	42	532	219	751	387	1,028	1,415
Ave.		8.5	62	561	291	853	420	1,004	1,429
sz†		0.9	6.6			69.6			141.5
<i>Puddled soil dried over hot plate‡</i>									
1	9.7		83	850	290	1,140	2,800	3,035	5,830
2	9.7		86	821	226	1,047	2,010	3,300	5,310
Ave.	9.7		84.5	836	258	1,094	2,405	3,168	5,570
sz§	0.75		12.9			82.7			475

\* Averages of three samples per ball.

† Standard error of the mean based on three items per mean, each item being the mean of two samples.

‡ Averages of four samples per ball.

§ Standard error of the mean based on four items per mean, each item being the mean of two samples.

### *Effect of organic materials on development of water-stable aggregates*

Ground cornstalks, ground alfalfa, and sucrose were mixed in 100-gm. samples of the soil at rates of 5 and 50 tons per acre, and the mixed samples were puddled and exposed to wetting and drying as described previously. The experiment was duplicated at the 5-ton-per-acre rate by a set kept sterile throughout the incubation period. The results are presented in table 3.

When the soil was not sterilized and organic matter was applied in amounts equivalent to 5 tons per acre, every treatment resulted in a significant decrease in the aggregates in the range 0.1 to 0.05 mm., the greatest decrease occurring in the sample receiving sucrose. For the larger sizes the results were inconsistent,

and only a few of the differences were great enough to be significant. It is noticeable, however, that in the unsterile set the organic materials resulted in numerically fewer aggregates in most cases as compared with the untreated soil, a tendency not apparent in the sterile set.

With some exceptions the results in the sterile set for the 5-ton rate could be said to be represented fairly well by the check. The slightly larger number of aggregates in the 0.1 to 0.05 mm. size for the sucrose treatment may be the

TABLE 3

*Effect of organic materials on the development of water-stable aggregates in puddled soil*  
Counts\* in thousands per gram

TREATMENT	>1 MM. AGGREGATES	1-0.5 MM. AGGREGATES	0.5-0.25 MM. AGGREGATES	0.25-0.1 MM. AGGREGATES	0.1-0.05 MM.		
					Aggregates	Sand grains	Total
Soil not sterilized							
No treatment.....	0	2.9	15	136	848	181	1,029
5 T./A. alfalfa.....	.4	3.0	14	79	700	141	841
5 T./A. corn stalks.....	0	1.3	17	123	681	164	845
5 T./A. sucrose.....	.2	1.4	21	130	568	124	692
50 T./A. alfalfa.....	.07	2.3	20	99	400	134	534
50 T./A. cornstalks.....	.3	2.1	12	65	332	94	426
50 T./A. sucrose.....	.2	2.0	4	24	172	70	242
Least highly significant difference.....	.2	2.0	8.6	41.7			220
Least significant difference.....	.3	1.6	6.0	30.0			158
Soil sterilized							
No treatment.....	0	1.4	13	117	470	107	577
5 T./A. alfalfa.....	0	1.1	13	135	483	86	569
5 T./A. cornstalks.....	0	0.5	13	129	537	137	674
5 T./A. sucrose.....	0	1.1	16	120	694	136	826
Least highly significant difference.....		2.2	7.7	55.6			310
Least significant difference.....		1.5	5.3	38.2			213

\* Averages of three replicates, each of which were sampled in duplicate.

result of the natural stickiness of undecomposed sucrose. At the 5-ton level the aggregation in the sterile set was generally less for all size ranges than was the aggregation of the corresponding soils of the unsterile set, although the differences were not significant except in the 0.1 to 0.05 size range. An outstanding exception was the sucrose sample, which showed more aggregates of the smallest size than did the corresponding unsterile soil.

At the 50-ton rate of application, the results were so amplified that the trends were more obvious. At this rate, all treatments resulted in an actual reduction in aggregation in all sizes less than 1 mm. except in the 0.5 to 0.25 mm. class for

alfalfa, although the differences were generally not significant in the sizes above 0.25 mm. Only in the sizes greater than 1 mm. was there an indication of better aggregation resulting from additions of organic materials, but at the dilutions poured, the density of the aggregates per microscopic field was too low to enable adequate sampling in this size range.

In order to obtain a more accurate estimate of the number of large aggregates present, a complete rerun of the unsterilized 50-ton-per-acre set was made and two dilutions were poured for counting, one the same as before and the other at

TABLE 4

*Effect of organic material on aggregation determined at densities that enable accurate sampling for all sizes counted*  
Counts\* in thousands per gram

TREATMENT	>2 MM. AGGREGATES	2-1 MM. AGGREGATES	1-0.5 MM. AGGREGATES	0.5-0.25 MM. AGGREGATES	0.25-0.1 MM. AGGREGATES	0.1-0.05 MM.		
						Aggregates	Sand grains	Total
No treatment.....	0	.270	5.5	70	87	373	64	437
Alfalfa.....	0	0	2.4	40	77	328	69	397
Cornstalks.....	0	.012	0.8	8	55	237	47	284
Sucrose.....	.046	.380	1.1	3	11.8	54	18	72
Least highly significant difference.....		.24	2.7	9.2	40.5			142
Least significant difference.....		.16	1.9	6.3	27.9			97

\* Averages of three replicates, each of which were sampled in duplicate.

TABLE 5

*Number of fibers per gram compared with aggregates per gram\**

		0.5-0.25 MM.	0.25-0.1 MM.	0.1-0.05 MM.
Alfalfa† {	Fibers.....	430	2,400	6,000
	Aggregates.....	40,000	77,000	397,000
Cornstalks† {	Fibers.....	170	1,800	1,450
	Aggregates.....	8,300	55,000	284,000

\* Averages of three samples.

† Rate of application 50 tons per acre.

a concentration that would give a high enough density of the larger particles (greater than 1 mm.) per microscopic field to ensure representative sampling. From the results in table 4, it can be seen that although alfalfa and cornstalks did not produce the same degree of aggregation as that developed in the untreated soil, the sucrose resulted in the best aggregation of particles greater than 1 mm. in size. Although the effects of the treatments are in the same directions as in the first test at the 50-ton-per-acre rate, they are not of the same magnitudes, a circumstance that probably reflects lack of complete control over the rate of wetting and of drying in the two runs.

Since a number of fibers were noticeable in the dishes poured from the samples treated with either alfalfa or cornstalks, it was feared that these fibers might be present in a concentration high enough to have a marked diluting effect. An actual count of the readily recognizable fibers showed that they constituted only a small portion of the particles present in each size group (table 5).

*Effect of organic materials on morphology of aggregates formed after puddling*

The aggregate analyses showed that marked differences in the soil structure resulted from different organic materials, the greatest differences occurring be-

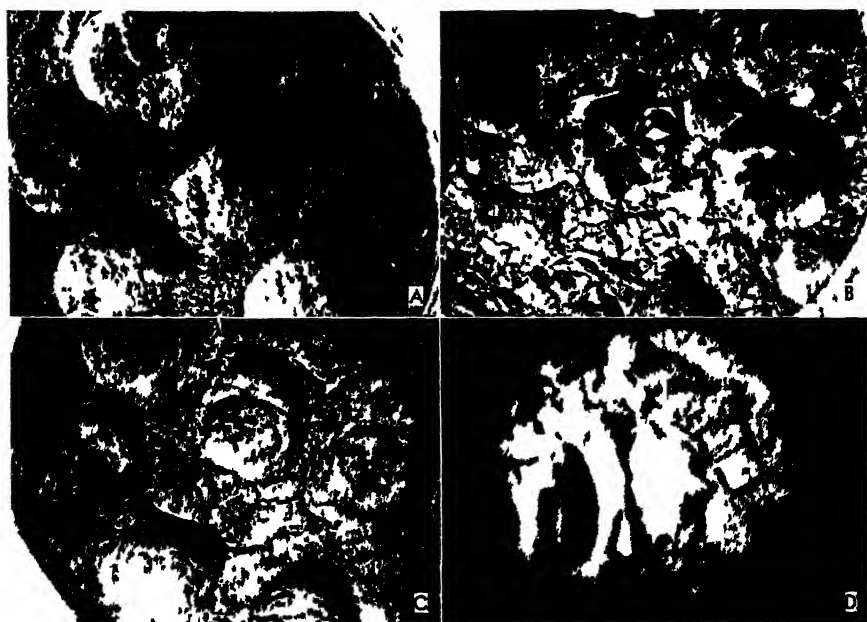


FIG. 1. TYPES OF AGGREGATION DEVELOPED FROM PUDDLED SOILS UPON WETTING AND DRYING

Organic materials applied at the rate of 50 tons per acre

A. Typically granular structure developed in puddled balls of soil treated with corn stalks.

B. Angular, blocky structure developed in puddled balls of soil treated with sucrose

C. Poorly aggregated balls of soil receiving sucrose but incubated under aseptic conditions.

D. Dense, angular aggregates of soil treated with sucrose (approximately  $\pm 5\times$ )

tween sucrose-treated soils and the other soils in the experiment. The soils receiving sucrose also showed definitely different morphological characteristics.

After the incubation period the soils treated with alfalfa and sucrose were all of the same light brown color as the check, but the soil treated with sucrose was black. Upon wetting after puddling, all the balls except those made from the sucrose-treated samples absorbed water rapidly, the drops disappearing from the surface by capillary adjustment, whereas the water drops lingered on the surface of the balls from the sucrose set until the whole surface became wet and shiny.

At the second wetting, many small cracks, which had appeared in all except the sucrose set, quickly closed from swelling, and a tendency toward exfoliation appeared in the sucrose set. Both the untreated soil and the cornstalk soil were easily wetted, but the alfalfa soil did not take the water up readily. The sucrose soil was still very hard to wet. On the third wetting a noticeably granular structure began to appear in all except the balls from the sucrose soil, which still showed very little swelling or granularity but which had begun to split into large angular blocks of tightly cemented plastic material. These morphological differences, which were noticeable at both the 5-ton and 50-ton rates of application, persisted throughout the wetting and drying process and are shown in figure 1. In the sterile set, however, there was less difference between the different samples.

Figure 1A depicts the soil treated with cornstalks as it appeared after wetting and drying 10 times. It is typical of the granular condition of all samples except those receiving sucrose. The angular, blocky structure of the sucrose-treated samples is shown by figure 1B. The effect of keeping the soil sterile during the incubation is seen in figure 1C, which shows sucrose soil treated similarly to that in figure 1B except for sterilization. In figure 1D the angular blocks of the unsterilized sucrose-treated soil are shown at approximately 4.5 magnifications.

#### DISCUSSION

Preliminary tests revealed that samples of the same soil would develop similar states of aggregation, if similarly treated, puddled, and exposed to wetting and drying. This uniformity of results seemed to justify the use of the procedure as the means of testing the relative effects of different organic materials on the ability of soils to become aggregated following puddling. The tests in the first part of the experiment, including those at the 5-ton-per-acre rate in both the sterile and the nonsterile set and the first set at the 50-ton rate, were all run at the same time under virtually identical conditions of wetting and drying. When the rerun was made, however, at the 50-ton rate of application, a new set of values was obtained. This was interpreted to reflect the effect of differences in wetting and drying conditions which could not be completely controlled with the equipment used.

Trends which were not apparent at the 5-ton rate of application were definite at the 50-ton rate. Although such an impractical rate of application would not be used in the field, the results very likely reflect the trends that should occur at ordinary rates. Why the alfalfa and the cornstalks, in general, did not produce such good aggregation as that which developed in the check soil is not known. Such results are contrary to common experience. Possibly the biological activity stimulated by the presence of the organic matter resulted in a weakening of the binding material already present in the soil. It is also possible that the often observed beneficial effect of organic matter on soil structure in the field has been largely the result of the binding action of such microbiological growth forms as mycelia, which could not contribute noticeably to the structure of the soils in the experiment because they were broken up by the puddling treatment after incubation had been completed.

The outstanding difference due to treatment was the quantitative and morphological nature of the aggregation developed where sucrose had been added at the rate of 50 tons per acre. When counts were made at concentrations great enough to ensure accurate sampling of the larger aggregates, sucrose was found to result in fewer aggregates smaller than 1 mm. and in more aggregates larger than 1 mm. The structure resulting from sucrose consisted of large angular blocks resembling angular nut structure accompanied by a mixed, discontinuous mass of very small aggregates and dispersed material. The blocks consisted of dense, fine-grained material. On the other hand, all the other samples exhibited a granular structure, with few very large granules and very little dispersed material. These results raise the question of what is good structure. Would the granular soil which rapidly absorbed water and which had more particles in the size classes between 0.05 and 1 mm., result in better moisture absorption and less erosion than the structure consisting of a greater number of large, compact, angular fragments and fewer aggregates in the intermediate sizes?

In view of the different rates of decomposition of materials involved, it is realized that the stage of decomposition in each treatment was not the same at 30 days. It might be that upon more complete decomposition the alfalfa and the cornstalks would produce structures more like that resulting from sucrose, which is more rapidly utilized by microorganisms. In spite of the variability in results at the 5-ton level for the sizes larger than 0.1 to 0.05 mm., there was evidence of reduced aggregation in the sterile set as compared with corresponding samples in the unsterile soil. This could be taken as an indication that biological activity was essential to the changes produced, provided the total effect was not due to the sterilization treatment itself.

The marked differences in structural morphology and in the size distribution curves of water-stable aggregates that resulted from sucrose as compared with the other treatments emphasize the need for refined methods of evaluating soil structure and for a better knowledge of what constitutes good structure.

#### SUMMARY

Development of aggregation was tested in samples of soil from the B horizon of Tama silt loam mixed with ground alfalfa, ground cornstalks, and sucrose at rates of 5 and 50 tons per acre, incubated for a month, puddled, and exposed to wetting and drying.

Preliminary tests revealed that it was possible for samples of the same soil to acquire somewhat similar states of aggregation following puddling if exposed to similar conditions of wetting and drying.

Except when the soils were incubated under aseptic conditions, ground alfalfa and cornstalks resulted in less aggregation, in general, than that which developed in the untreated soil. At the 50-ton rate cornstalks produced less aggregation than alfalfa. These results may mean that at the stage of decomposition represented by this experiment, the incubation of these materials in the soil had resulted in changes that depressed the capacity of structure to form following puddling.

At the 50-ton rate sucrose produced more aggregates larger than 1 mm. than

occurred in any of the other treated or untreated soils, but in most cases it resulted in fewer aggregates smaller than 1 mm. The aggregates in the sucrose-treated samples were angular and blocky and were composed of a dense, compact ground mass, whereas the aggregates in all other samples were granular and were composed, in turn, of all grades of smaller sized granules. The structural units in the sucrose samples were wetted with difficulty and did not exhibit much swelling, whereas the structural units in all the other samples absorbed water readily and exhibited marked swelling.

What would be the agricultural significance of the outstanding differences in the morphology and in the size distribution of the aggregates that formed in the sucrose-treated soil in comparison with the other soils is not known. The results of the study point to a need for careful characterization of soil structure in order that the relation of cultural practices to the physical condition of the soil may be established with greater accuracy and definiteness.

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# SOME SOLODIZED SOILS OF THE RED RIVER VALLEY<sup>1</sup>

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Intrazonal soils develop when some local condition interferes with the normal soil-forming processes and forces a departure from the normal or zonal type. In the Minnesota portion of the Red River Valley varying quantities of soluble salts in localized areas produced conditions that have given rise to a series of intrazonal soils, which are now found among the normal chernozems and chernozemlike soils of the valley.

When the waters of Glacial Lake Agazzi receded, a vast area of nearly level terrain was exposed. On this plain were areas of varying size on which shallow lakes and swamps persisted and a high ground-water table was common. Since surface drainage was imperfect, the only escape for water from many areas was solar evaporation, and under these conditions the dissolved salts accumulated as the lakes, ponds, and swamps became dry. The soils were either salinized<sup>3</sup> or alkalized, depending on the amount of salts that accumulated.

In some soils examined, the salts consisted of sulfates and hydrogen carbonates of calcium, magnesium, and sodium (14). Sodium sulfates and the three hydrogen carbonates were present in relatively small amounts; therefore, the bulk of the salts consisted of  $\text{CaSO}_4$  and  $\text{MgSO}_4$ . Until excessive amounts of  $\text{CaSO}_4$  had been removed from the solum by leaching, solonetz formation was repressed by the protective influence of calcium ions (15). Solonchak soils now occur much more generally near the eastern outer side of the valley, whereas solonetz in various stages of solodization, and possibly solodi soils, are to be found in the central part.

The present study is concerned with three groups of solodized soils which may represent different stages in the solodization process.

## MATERIALS AND METHODS

The soils of group I are the least solodized of the three groups. In this group are five of the six profiles of solodized solonetz for which Rost (14) has already reported many data.<sup>4</sup> The soils contain soluble salts in the B horizon, which is further characterized by a columnar structure. They occur in variably sized spots, usually small, and appear to lie on the slopes of very slight depressions.

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<sup>3</sup> The terms *salinization*, *desalinization*, *alkalinization*, and *solodization* have been defined by Nikiforoff (12, p. 786) and by Kellogg (8, p. 23-25).

<sup>4</sup> Exhaustion of laboratory samples necessitated omission of Rost's profile 2 from this study.

The soils of groups II and III are distributed similarly to those of group I, in that they usually occur in small areas or spots scattered throughout areas of normal soil. Instead of being found on the rims of depressions, however, they occur more commonly in small depressions, and they are best displayed in such situations. They may occur, however, on essentially level terrain. One sizable area occupies part of a level plain in Clay County. The area embraces approximately 8 square miles and lies in the southwestern and northwestern corners of Kragnes and Oakport Townships, respectively. Although not all the soils of the area are intrazonal, a very considerable part would be so classified. Five scattered profiles on this plain and seven others in shallow land-locked depressions in Wilkin and Norman Counties were sampled for the present study.

The morphology of these 12 profiles resembles that of the solodized solonetz of group I. The profiles are characterized by an  $A_1$  horizon that is black in color, with a granular structure at the top which becomes lamellar toward the bottom. Light-colored silica-coated particles are observed in this horizon in some profiles. The texture varies from silt loam to clay loam. The  $A_2$  horizon is light gray to ashy gray in color and lamellar in structure. The B horizon is black to very dark gray and is very compact and hard when dry and sticky when wet. In structure it is nutlike to coarsely blocky. It differs in appearance from the B horizon of the soils of group I in that it is slightly lighter in color and lacks the columnar structure. From the lower part of the horizon there is a gradual transition, usually within 4 inches, to the olive-gray clay or silty clay parent material. Soluble salts have been completely leached from the profile.

After representative profiles were located in the field they were fully exposed and studied before sampling. When horizons were not more than 6 inches thick, one sample was taken. For those 7 or more inches thick, two or more samples were taken, each being as near to 4 inches as possible. Thus the thickness of the sections sampled ranged from  $3\frac{1}{2}$  to 6 inches.

The texture of the samples is expressed as the moisture equivalent. The reaction, expressed as pH, was determined by means of the glass electrode.

In carbonate-free samples exchangeable cations were removed by extraction with 1 *N* ammonium acetate. Exchangeable hydrogen was determined by the method proposed by Maehl (10). Calcium, magnesium, sodium, and potassium were determined by standard methods. Samples containing carbonates were extracted with a 70 per cent alcoholic solution of 1 *N* ammonium acetate, and exchangeable cations determined as in the carbonate-free samples.

Soluble silica and alumina were extracted with a 5 per cent solution of KOH in a manner similar to that suggested by Gedroiz (4). Ten grams of soil was treated with 25 ml. of 1 per cent HCl and allowed to stand for 3 hours with occasional stirring. The soluble material was then filtered off and the filtered soil digested on the steam bath with 50 ml. of 5 per cent KOH for  $1\frac{1}{2}$  hours with occasional stirring. The digested material was filtered, and silica and alumina were determined in the filtrate by standard methods. The amount of silica necessary to convert the  $Al_2O_3$  to  $Al_2O_3 \cdot 2SiO_2$  was then deducted from the total

SiO<sub>2</sub>. Considerable amounts of organic matter were dissolved by the KOH and any silica or alumina contained in this is included in the amounts reported. For this reason the determination is not so exact as would be desirable.

The 17 profiles under consideration have been arranged, on a chemical and morphological basis, into three main groups. Since the profiles were fairly similar morphologically, the division into groups has been largely on chemical characteristics. The factors given consideration were the presence or absence of soluble salts, the reaction, and the amounts and distribution in the profile of soluble silica and exchangeable hydrogen, calcium, and magnesium.

The criteria used in establishing the three groups follow:

*Group I.*

Soluble salts are present in the B horizon.

The A horizon is acid, but the B shows little or no acidity.

Exchangeable hydrogen is confined almost exclusively to the A horizon with a higher proportion in the A<sub>2</sub> than in the A<sub>1</sub>.

The amount of exchangeable magnesium exceeds that of the exchangeable calcium in the B horizon.

Soluble silica in all horizons is lower than that in corresponding horizons of groups II and III.

*Group II.*

The solum is leached of soluble salts.

The acid reaction extends well into the B horizon, although the latter is usually only mildly acid. The acidity decreases with depth in the profile.

Exchangeable hydrogen usually is found in all parts of the solum and always is highest in the A horizon.

Exchangeable calcium in the B horizon is distinctly higher and exchangeable magnesium markedly lower than in the profiles of group I.

Soluble silica in the A horizon is very high, and the amount in the A<sub>1</sub> is greater than that in the A<sub>2</sub>.

*Group III.*

The profile is free of soluble salts.

The A<sub>1</sub> horizon is only mildly acid; the B<sub>1</sub> and B<sub>2</sub> horizons are more acid than any others in the profile.

Exchangeable hydrogen is lower in the A horizon than in the same horizon in groups I and II. As percentage of total cations, it is considerably lower in the A<sub>1</sub> than in the A<sub>2</sub>.

Exchangeable calcium expressed as percentage of total cations is distinctly higher in the A<sub>1</sub> horizon than in the A<sub>1</sub> of groups I and II.

Soluble silica in the A<sub>1</sub> horizon is about the same as that in the A<sub>2</sub>. Amounts in the latter usually are higher than in the same horizon of members of groups I and II.

#### EXPERIMENTAL RESULTS

To avoid unnecessary duplication of data, analyses of individual profiles are not presented. Instead, table 1 gives an average analysis of the horizons of 17 profiles as they seemed to fit into any one group. The data in group I, then, represent an average analysis of five profiles; those in groups II and III, an average of six profiles each. The inclusion of the three groups into one table facilitates comparison of the data.

In discussing the chemical characteristics of the various groups, it should be pointed out once more that there is a major difference between group I and the

other two groups that is not evident from the data presented. This difference lies in the fact that the soils of group I have, somewhere in the profile, an accumulation of soluble salts (14).

On the whole, the total depth of soil differs little among the groups, the average being about 3 feet. Though the  $A_1$  of group III is shallower than that of groups I and II, the  $A_2$  and  $B_1$  horizons show a progressive increase in thickness from group I to III. This is an indication of a progressive increase in solodization.

TABLE 1

*Texture, reaction, exchangeable cations, and soluble  $SiO_2$  and  $Al_2O_3$  of three groups of solodized soils*

HORIZON	THICKNESS	TEXTURE AS MOISTURE EQUIVALENT	REACTION	TOTAL EXCHANGE CAPACITY	EXCHANGEABLE CATIONS, PERCENTAGE OF TOTAL					SOLUBLE $SiO_2$	SOLUBLE $Al_2O_3$	EXCESS $SiO_2$ OVER $Al_2O_3 \cdot 2SiO_2$
					H	Ca	Mg	Na	K			
	<i>inches</i>	<i>pH</i>	<i>m.e.</i>						<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	
Group I												
A <sub>1</sub>	6.5	31.3	5.9	33.8	20.7	51.0	25.5	1.4	1.3	6.05	0.129	5.90
A <sub>2</sub>	4.5	19.2	6.0	16.6	22.0	41.1	32.4	3.5	1.1	4.48	0.164	4.29
B <sub>1</sub>	4.0	36.0	7.1	36.9	6.8	24.3	64.0	3.5	1.4	2.37	0.405	1.90
B <sub>2</sub>	4.8	34.9	7.6	38.2	2.7	31.0	63.9	2.7	0.7	1.94	0.296	1.59
BC	4.8	33.1	7.9	39.0	0.0	42.2	55.3	1.6	1.0	1.65	0.201	1.42
C	8.7	31.8	8.0	35.0	0.0	59.1	38.6	0.5	1.8	2.24	0.137	2.08
Group II												
A <sub>1</sub>	7.0	33.1	5.9	31.7	15.7	59.4	21.2	0.7	3.0	9.13	0.102	9.01
A <sub>2</sub>	5.7	23.8	6.3	19.6	12.9	56.0	25.9	1.3	4.0	5.90	0.183	5.68
B <sub>1</sub>	4.7	31.9	6.4	33.3	8.8	58.2	28.7	0.9	3.5	3.05	0.335	2.65
B <sub>2</sub>	10.0	35.5	6.6	37.1	7.3	60.3	28.5	0.7	3.3	3.30	0.314	2.93
BC	5.6	35.1	7.2	35.3	4.5	63.2	28.5	0.7	3.2	4.34	0.208	4.09
C	5.8	35.3	7.5	34.3	2.7	65.2	28.2	0.9	3.0	4.44	0.140	4.28
Group III												
A <sub>1</sub>	5.2	42.1	6.7	48.7	7.7	68.4	19.8	0.4	3.9	7.26	0.082	7.17
A <sub>2</sub>	7.2	31.2	5.9	30.6	16.8	55.5	23.3	0.8	3.6	7.27	0.128	7.12
B <sub>1</sub>	5.3	36.1	5.3	40.8	16.6	50.5	29.3	0.8	2.9	4.38	0.222	4.12
B <sub>2</sub>	7.3	38.9	5.4	42.1	12.7	51.8	31.9	0.9	2.8	3.82	0.258	3.52
BC	4.0	38.2	6.3	39.5	6.0	55.7	34.6	0.9	2.8	3.62	0.232	3.35
C	7.3	36.7	7.7	34.6	0.9	59.9	35.8	0.9	2.6	3.43	0.168	3.23

The moisture equivalent has been used extensively as a measure of soil texture. Although it is recognized that differences in organic matter content and probably in the nature of inorganic colloidal matter affect the determination of moisture equivalent, the use of the expression here is felt to be suitable for the purposes of this study. The similarity of the figures obtained for the various groups indicates the uniformity in texture of the profiles. There is a distinct drop in the moisture equivalent of the  $A_2$  horizon of all profiles, compared to the  $A_1$

and B<sub>1</sub>. The higher figure in the B horizon indicates an eluviation of material from the A. A close inspection of the data suggests a somewhat deeper eluviation of material in moving from group I to III.

The differences in pH exhibited in the horizons of the various profiles were given considerable weight in allocating a profile to any one group. There are evident differences in the degree and distribution of acidity between the groups. Group I is acid in the two surface horizons but basic in the B and C horizons. Extensive leaching of bases has not extended beyond the A<sub>2</sub> horizon. In group II the same trend is shown with respect to increase in basicity with depth in the profile, but leaching has been more extensive and the neutral point is not exceeded until the BC horizon is reached. Group III presents a sharp departure from the trend of increasing basicity with depth. The A<sub>1</sub> horizon is only slightly acid, the A<sub>2</sub> is more so, and the B<sub>1</sub> and B<sub>2</sub> horizons are the most acid in the profile, with pH values of 5.3 and 5.4, respectively. The acidity extends into the BC horizon. The only basic horizon in the whole profile is the C. It would appear that leaching has proceeded further or has been more extensive in this group than in either I or II. Judging from the fairly acid A<sub>1</sub> horizons of groups I and II, it would be reasonable to believe that some time in the past the A<sub>1</sub> horizon of group III had been more acid than it is at present. Some agency, probably vegetation, has been sufficiently active to return bases at a faster rate than they can be removed.

Little comment need be made on the total content of exchangeable cations in the various groups other than to point out the reduced number of milliequivalents in the A<sub>2</sub> horizon compared to the A<sub>1</sub> and B horizons. This could be expected in view of the lower amount of colloidal material, both organic and inorganic, in the A<sub>2</sub> horizon. Extensive decomposition and removal of material have taken place in this layer. The organic matter in the A<sub>1</sub> horizons increases the base-exchange capacity, and eluviated inorganic matter deposited in the B horizons accounts for the higher exchange capacity there.

Before exchangeable hydrogen is discussed, it might be well to point out that recent data of Gammon *et al.* (3) have shown that ammonium acetate (the extractant used in the base-exchange studies reported herein) tends to give apparently excessive amounts of exchangeable hydrogen. Thus, although the amounts reported in this study may be greater than they should be, they probably are comparable.

The trends shown by exchangeable hydrogen parallel rather closely those shown by the pH. Exchangeable hydrogen is high in the A<sub>1</sub> and A<sub>2</sub> horizons of groups I and II and decreases with depth in the profile. A higher content of hydrogen to a greater depth is shown in group II as compared to group I. In group III the exchangeable hydrogen is highest in horizons A<sub>2</sub>, B<sub>1</sub>, and B<sub>2</sub>. In keeping with a pH of 6.7, exchangeable hydrogen in the A<sub>1</sub> horizon is fairly low, less than half that found in the A<sub>1</sub> of group I or II. Whereas hydrogen has replaced some base or bases to a considerable depth in the profile, extending even below the B<sub>2</sub> horizon, calcium has in turn replaced hydrogen in the A<sub>1</sub>.

The greatest differences in the exchangeable calcium contents of the various

groups are to be found in the reductions in horizons  $B_1$  and  $B_2$  of group I. This difference is due to the predominance of exchangeable magnesium in these two layers. A similar, but not so pronounced, effect is shown in the BC horizon. A reduced exchangeable calcium content in the  $B_1$  and  $B_2$  horizons of group III coincides with a higher exchangeable hydrogen, and not magnesium as in group I.

The dominant exchangeable cation in the  $B_1$ ,  $B_2$ , and BC horizons of group I is magnesium. That such a condition is not confined to intrazonal soils in Minnesota is pointed out subsequently in the discussion. Such a situation is not evident in the soils of groups II and III, in which the dominant cation throughout the profile is calcium. There is just a suggestion of an accumulation of magnesium in the  $B_1$ ,  $B_2$ , and BC horizons of group II, in that the contents are higher than that of the parent material. Though it is questionable whether small differences are significant, nevertheless in group III no accumulation of magnesium is evident anywhere in the profile, the content increasing progressively with depth.

Group I contains a few milliequivalents more exchangeable sodium in the various horizons than do groups II and III, in which the sodium content is negligible. Horizons  $A_2$  and  $B_1$  of group I contain 3.5 m.e. of sodium, but it is doubtful whether this small amount is sufficient to play the role Gedroiz assigns to it in the formation of the type of intrazonal soils under discussion.

The position with respect to exchangeable potassium is just the opposite to that shown by sodium. In other words, exchangeable potassium in groups II and III, 3 to 4 m.e., is higher than that in group I, which varies between 1 and 2 m.e. The amounts are small, of course, in all groups, but nevertheless differences between the groups would seem to be significant. Weathering has occurred to a greater extent in the profiles of groups II and III, with a consequent greater destruction of silicates, liberating potassium. Numerous studies have shown that potassium is readily and firmly fixed in the exchange complex, and it is therefore no anomaly that greater amounts of exchangeable potassium should be found in the profiles of groups II and III. Were the exchangeable potassium contents three to four times those shown, some part in the formation of solodi soils might be ascribed to this cation, since it is an alkali cation which reacts similarly to sodium.

The method of treatment used in this study to obtain so-called soluble silica and alumina yields considerable amounts of the latter. The differences between the groups are not great, though a reduced content may be observed in the intermediate horizons of group III, compared to groups I and II. There is an evident accumulation of alumina at some point in all profiles. In group I it is largely in the  $B_1$  horizon; in group II, in the  $B_1$  and  $B_2$ ; and in group III, in the  $B_1$ ,  $B_2$ , and BC, with the greatest amount in the  $B_2$  rather than the  $B_1$ . Disintegration of the mineral complex has taken place and alumina has moved down in the profile. Indications are that progressively greater weathering and eluviation have occurred in going from group I through II to III.

Gedroiz considered that 5 per cent KOH dissolved other than strictly amorphous silica, but if the soluble alumina is combined with sufficient silica to satisfy

their ratio as in kaolinite ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ), then any silica over and above this could be considered amorphous silica. Accordingly the figures in the last column of table 1 indicate the silica remaining after a sufficient quantity has been subtracted to combine with alumina as indicated.

Appreciable amounts of soluble silica are apparent in all horizons of the three groups. The A horizons contain approximately two to three times the quantities found at lower depths. If this determination can be taken as an indication of the weathering that has occurred in solonetz and solodi soils, destructive processes have been active in the surface horizons. Differences in soluble silica, which may or may not be significant, are evident between groups. All horizons of group II have higher soluble silica contents than those of group I, with considerably more in the A horizon. In group III the soluble silica is more evenly distributed throughout the profile. To explain this it is assumed that either a slightly different type of weathering has occurred in group III as compared with group II, or else the former has passed through the stage now represented by the latter and the silica in the  $A_1$  and  $A_2$  horizons has been more evenly distributed by mechanical movement. No ready explanation can be given for the drop in horizons  $B_1$  and  $B_2$  of group II compared to the A, BC, and C horizons.

#### DISCUSSION

Rost, in a previous paper (14), discussed the profiles of group I, the average data for which are shown in table 1. He pointed out that though these profiles met the requirements morphologically for a solodized solonetz, they did not agree chemically with Gedroiz' characterization of such profiles in that they contained only minor amounts of exchangeable sodium. On the other hand, in the B horizon at any rate, magnesium was the dominant exchangeable base. Such a condition has been observed in solonetz soils by other workers. Storie (18) and Kelley (6) in California, Ellis and Caldwell (2) in Manitoba, and Mitchell and Riecken (11) in Saskatchewan reported data on morphological solonetz soils in which the exchangeable sodium content was low.

De'Sigmond (16) has proposed a classification of soils based largely on chemical characteristics. In the humo-siallites under main group II (soils of mixed origin), sodium soils were included as one of three orders. De'Sigmond characterized the sodium soil order as having an ABC profile, a stable colloid dispersion, a pH of 6.5 to more than 10.0, and an exchangeable sodium content of more than 12-15 per cent of the total exchangeable bases or a sodium salt content of more than 0.15 per cent. Why the figure 12-15 per cent was chosen is not clear, unless that content of exchangeable sodium is necessary or sufficient in minimum to give rise to solonetz soils in a manner outlined by Gedroiz (4). Though de'Sigmond does not always agree with Gedroiz in the manner in which sodium carbonate and sodium hydrogen carbonate may be formed in the soil, he is in substantial agreement with the importance of the sodium cation in giving rise to the typical profiles of alkali soils.

An inspection of the data reported by Kelley (6) shows that several of the profiles have sufficient exchangeable sodium to be included among de'Sigmond's



sodium soils. Stalwick (17), in an investigation of five Saskatchewan solonetz soils, found 6.50 to 21.93 per cent of the total exchangeable bases in the B<sub>1</sub> horizon to be sodium. Two of these profiles contained 13.16 and 21.93 per cent exchangeable sodium in the B<sub>1</sub> horizon, sufficient to be included in de'Sigmond's sodium soils. MacGregor (9) made a study of the water-soluble salts and exchangeable bases in a number of normal soils and morphological solonetz soils of Alberta. The variation in exchangeable sodium as percentage of bases in the various horizons of 20 solonetz and 4 normal soil profiles was found to be as follows:

Horizon	Solonetz soils	Normal soils
A <sub>1</sub>	2-12	2-3
A <sub>2</sub>	3-16	2-2
B <sub>1</sub>	1-17	1-2
B <sub>2</sub>	1-21	1-2
C	1-6	

It can be seen that some, at least, of the solonetz soils MacGregor examined have sufficient sodium to be called "sodium soils" according to de'Sigmond's classification.

In the solodized solonetz soils reported herein and also in the solonchak soils studied by Rost and Chang (15), the exchangeable sodium in no instance approaches the limits set by de'Sigmond. Furthermore in only one profile was there sufficient sodium to meet the other requirement of a sodium soil, viz. 0.15 per cent of sodium salt.

If it is assumed that a minimum of 12-15 per cent exchangeable sodium is sufficient to give rise to solonetz soils, then there is evidence that Gedroiz' theories may hold in the formation of some California, Alberta, and Saskatchewan solonetz soils. But there is no evidence that sodium has played a similar role in Minnesota soils, insofar as analyses of solonchak, solodized solonetz, and solodi soils have been able to show. What the situation would be with respect to true solonetz soils is not known, since none have as yet been investigated in Minnesota. It is recognized that the lack of exchangeable sodium is no evidence that sodium did not formerly play its part in the formation of solodi soils. Gedroiz (4) and de'Sigmond (16) fully appreciate the fact that solodi soils, in the course of formation, may have lost the greater part of their replaceable sodium.

Because of the high exchangeable magnesium found in Minnesota solodized solonetz and in solonetz reported from Saskatchewan (11), Manitoba (2) and California (6), the suggestion has been made that this cation may be responsible for the dispersion of these soils and the resultant solonetzic characteristics. No experimental evidence has been forthcoming to substantiate this suggestion. Sushko and Sushko (19) have reported data which indicated that magnesium is more like calcium than sodium in its effect on the dispersibility and filterability of soils.

Riecken (13) has discussed the low ratio of calcium to magnesium in the B<sub>1</sub> horizon of solonetz soils, and has asserted that the status of the exchangeable bases

in the illuvial horizon of the solonetz soils has been established because of the relationship existing between the relative additions of bases by the vegetation and mineral weathering to the exchange complex. The development of a claypan favors weathering of the horizon above, and the magnesium weathered from this layer is greater than the calcium supplied by vegetation, thus allowing magnesium to accumulate (13). It is possible in this way to account for the dominance of exchangeable magnesium in the lower horizons of solonetzic soils without assuming it to have played the role attributed to sodium.

If magnesium is not instrumental in the formation of solonetz soils, and only sodium is, the absence of the latter in many solonetz soils means that this cation has been active in the past but has since been lost, in which case the soils examined have not for some time probably, and certainly are not at the present time, being solonized or solodized. On the other hand, if the absence of sodium means that its presence is not essential for solonetz formation, some other agency must be sought to account for these soils. Bray (1) has outlined his theories on the formation of a claypan in soils. He postulated that the colloidal material is formed in place and remains except for downward movement of the superfine colloid. Slight unsaturation and the mechanical force of rainfall may cause dispersion of this superfine material, and leaching waters filtering through cracks and root channels move the material to deeper horizons. Bray's hypothesis suggests a process by which the heavy-texture B horizon of solonetz soils could be formed. Then under such conditions impeded drainage and greater weathering in the A horizon would result.

If, for lack of sodium, solodization has ceased in the group I profiles, then further changes toward a solodi soil would not be expected. It would seem logical, however, to postulate that, as drainage improves, soluble salts would be removed from these profiles. Further leaching would remove exchangeable bases to be replaced by hydrogen and calcium. Sodium might be reduced to the contents shown by groups II and III, and magnesium replaced largely by calcium, as has already taken place in the  $A_1$  and  $A_2$  horizons. A source of calcium would be provided by the decomposition of the parent material and return by vegetation. Such a return is indicated by the pH, the comparatively low exchangeable hydrogen, and the high exchangeable calcium in the A horizons of group III.

The soils of groups II and III satisfy fairly well both the morphological and the chemical requirements of solodi soils as outlined by Gedroiz (4) and de'Sigmond (16). Hydrogen is present to a considerable extent in the exchange complex, indicating extensive leaching. The contents of soluble silica meet Gedroiz' requirements in this respect, and, as a matter of fact, few of the solodi soils on which Gedroiz reported have as high a content of soluble silica as that found in the present study.

Gedroiz laid considerable stress on the importance of soluble silica as an indicator of the solonization and solodization processes. Though a similarity was recognized between the solodi and the podzol profile, Gedroiz found little or no soluble silica in podzols. De'Sigmond, on the other hand, placed little

importance on alkali-soluble silica as an indicator of solodization and maintained that the silica found is simply the result of previous decomposition by HCl. Contrary to the findings of Gedroiz, de'Sigmond (16) found up to 2 per cent of soluble silica in a podzol profile. A 5 per cent KOH solution was used, but previous treatment with HCl was not indicated.

Although it is possible that, because of small differences in their manner of formation, groups II and III may represent two different types of solodi soils, it is also possible that, as leaching progressed, hydrogen would move down in group II until a picture somewhat analogous to that of group III would be shown. The exchangeable magnesium, instead of remaining high in the B<sub>1</sub> horizon as it is at present, would be replaced by hydrogen or calcium until a progressive increase with depth would result, as shown by the exchangeable magnesium in group III. Finally calcium, returned to the surface by vegetation, would replace hydrogen, and a saturated soil would result.

The data as shown have led to the inference that the three groups of soils represent progressive stages or degrees of solodization. There is no evidence, however, to show that these soils formerly were solonetz and solonchak, and conversely, no proof that they were not. The general inference, based mainly on hypotheses brought forth by Russian workers, is that alkali soils pass through three stages, from solonchak to solonetz to solodi (5). Nikiforoff (12) is not in full agreement with the theories of Gedroiz and de'Sigmond that solonchak, solonetz, and solodi must necessarily represent three continuous stages and that one stage leads inevitably to the next. He points out that the true solodi is a typical soil of depressions and that "the most typical solonetz is found not infrequently in such locations where neither solonchak nor, and especially, solodi were ever found." This suggests the possibility, he believes, that solonchak, solonetz, and solodi may really be genetically independent soil formations, the development of which is governed in each case by different local factors.

If the aforementioned postulates hold, and since the fact that the soils of groups II and III were depression soils and the profiles of group I were taken on the rims of depressions lends credence to Nikiforoff's views, then it may be that the soils of group I would never become true solodi soils or show the chemical characteristics evident in groups II and III.

Some question may be raised as to the use and application of the terms *solodized solonetz* and *solodi* throughout this paper. As Kelley and Shaw (7) have already pointed out, the application of the terms *solonetz* and *solonchak* to some of our intrazonal soils is not clear. Apparently in some instances the Russian workers themselves disagreed as to the use of the terms, depending on the chemical and morphological characteristics of the soils in question. De'Sigmond (16) asserts that so-called *solonetz* soils are only truly *solonetzic* in the Russian meaning of the term when the soil contains sodium in the adsorption complex. If sodium is not present (magnesium dominant), then the term *solonetz* refers only to the structure of the soil and does not correspond to the the original idea expressed by the Russian word.

## SUMMARY

A study is reported of the characteristics of samples from 17 profiles of intrazonal soils from the Minnesota portion of the Red River Valley. The soils were divided, on the basis of their morphological and chemical characteristics, into three groups consisting of five, six, and six profiles, respectively.

The structure of the B horizon of group I differed somewhat from that of groups II and III, but otherwise the morphology of these soils was much alike. Thus the separation into groups was made largely on a chemical basis.

Chemical characteristics used in separating the groups were the presence or absence of soluble salts, pH, exchangeable cations, and soluble silica and alumina.

The presence of soluble salts in the profiles of group I facilitated their separation from the profiles of groups II and III and led to the designation of the former of *solodized solonetz*. The profiles of groups II and III were more acid to a greater depth than those of group I and contained more soluble silica. Exchangeable sodium and magnesium were higher in the profiles of group I than in those of groups II and III.

Groups II and III were differentiated mainly on the extent to which leaching had occurred, as indicated by the pH and the exchangeable hydrogen.

The chemical and morphological characteristics of the profiles of groups II and III were in substantial agreement with those of solodi soils reported by Gedroiz.

It was suggested that the profiles of groups I, II, and III represented a progressive increase in the solodization process, despite the absence of a destructive cation such as sodium.

There was some evidence that calcium is being returned to the surface in the profiles of group III, and it was suggested that eventually the exchange complex of these soils would become calcium-saturated.

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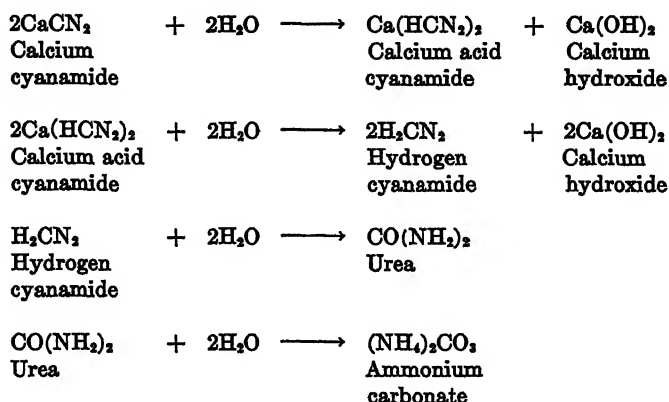
# EFFECT OF SOIL MOISTURE AND RAINFALL ON CHEMICAL TRANSFORMATIONS IN CYANAMID GRANULES<sup>1</sup>

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The results of investigation of the decomposition of Cyanamid in the soil, summarized by Pranke (7), McCool (6), Williams (10), Buchanan and Barsky (1), Smock (9), Crowther and Richardson (2), and Fink (3), lead to the conclusion that the chemical changes which the calcium cyanamide of the commercial product<sup>3</sup> undergoes when properly distributed on good agricultural soils are a simple physicochemical hydrolysis through calcium acid cyanamide and hydrogen cyanamide to urea, as expressed by the following reactions, and the usual biochemical ammonification of the urea:



The physicochemical reactions are catalyzed by numerous normal constituents of fertile soils, among which are the zeolites prehnite and apophyllite; various manganese, iron, and aluminum compounds; the clays in general; and organic colloids.

Decomposition of calcium cyanamide in the soil takes the foregoing normal course at the usual pH range of good agricultural soils, from moderately acid to slightly alkaline, and in the presence of catalysts and moisture. If, however, the soil in spots is rendered strongly alkaline—pH 8 to 12—by uneven distribution of the calcium cyanamide, the intermediate product hydrogen cyanamide,  $\text{H}_2\text{CN}_2$ , tends to polymerize to dicyandiamide,  $(\text{H}_2\text{CN}_2)_2$ .

<sup>1</sup> Contribution from the department of horticulture, Missouri Agricultural Experiment Station, Columbia, Missouri, Journal Series No. 879. This investigation was supported by a fellowship grant from the American Cyanamid Company.

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<sup>3</sup> The commercial product Cyanamid is made up largely, but not entirely, of calcium cyanamide.

These conclusions are based on investigations conducted with pulverized Cyanamid. Use of Cyanamid in granular form introduces a new factor, since obviously not all the calcium cyanamide in a granule can be brought into as close physical contact with catalysts in the soil as can that in pulverized Cyanamid. The ensuing transformations may be considered somewhat similar to those that take place when Cyanamid is stored (5) or when it is used in mixtures with other fertilizer materials (4).

The use of Cyanamid in orchard fertilization has given satisfactory results in most cases. When soils lack the necessary catalysts to bring about rapid transformation, or where moisture conditions do not favor rapid decomposition, however, transformation products toxic to plants accumulate. It is desirable therefore that these transformations take place as rapidly as possible. The speed of movement through soil and the efficiency in absorption by the roots of broadcast applications of granular Cyanamid to fruit trees have been found to be influenced by the precipitation immediately following the spreading of the fertilizers (8). When heavy rains fall soon after the Cyanamid is applied, the rate of absorption of nitrogen is almost as rapid as that from ammonium sulfate or sodium nitrate. When dry weather follows the fertilizer application, however, the Cyanamid granules become coated with white crystals and remain visible for months on top of the ground. Under these conditions the quantity of nitrogen absorbed by the trees is much below that absorbed when rainfall is higher. Analyses of these granules reveal that, when they remain on the surface of the ground for some time, much of the nitrogen is changed to dicyandiamide, which is of little immediate value to the trees. Detailed investigations were carried out to determine the nature and the rate of these transformations as influenced by soil moisture and rainfall conditions.

#### MATERIALS AND METHODS

Thoroughly screened and mixed Memphis silt loam surface soil was weighed into 3- by 5-foot field plots 7 inches deep. The plots were covered by paraffined cloth that protected them from rainfall but allowed free circulation of air. The soil was brought to approximately 20 per cent moisture, 16 gm. of nitrogen was added in each of the following fertilizers, and water applications were made as indicated:

- Plot 1—Ammonium sulfate was spread on the surface. Water was withheld for 14 days and then added by sprinkling at 4-day intervals in amounts absorbable in 15 minutes.
- Plot 2—Granular Cyanamid was spread on the surface. Moisture applications were similar to those on plot 1.
- Plot 3—Granular Cyanamid was spread on the surface. The plot was lightly sprinkled with water after 4, 8, and 12 days. After 2 weeks it was given the same moisture treatments as plot 2. On the second replication the fertilizer was worked into the soil to a depth of 2 inches and given the same moisture treatments as plot 2.
- Plot 4—Granular Cyanamid was spread on the surface. Water was added immediately in a quantity absorbable in 30 minutes, followed by sprinkling at 4-day intervals in amounts absorbable in 15 minutes.

The plots were sampled at 4-day intervals with a small tube sampler. The Cyanamid granules on top of the sample cores from plots 2, 3, and 4 were carefully removed and saved for analyses. The soil samples were immediately dried in a forced draft oven at 35°C. Determinations were made for moisture, total nitrogen, cyanamide nitrogen, dicyandiamide, urea, ammonia, and nitrates. The granules also were analyzed for these constituents and in addition for total calcium, water-soluble calcium, and total carbonates.

A study was conducted also with a 50-gm. sample of granular Cyanamid placed on a 40-mesh brass screen  $\frac{1}{8}$  inch above bare moist soil and protected from rain but exposed to atmospheric moisture and free circulation of air. At intervals, the granules were removed from the screen and weighed, a 1-gm. sample was removed, and the fertilizer was returned to the same position. The granule samples were shaken in sandpaper-lined vials for 30 minutes, which removed most of the outside white crust. Analyses were made for carbonates, calcium, and nitrogen compounds in both the inner and outer portions of the granules. The results were compared with those obtained on granules collected and analyzed in previous orchard experiments (8).

The effects of atmospheric conditions on the formation of encrustations were further studied on Cyanamid granules treated in a closed chamber for alternating 10-day periods with atmospheres of moist carbon dioxide and moisture-free air.

#### RESULTS

The rates of ammonia and nitrate production in the covered plots were similar to those obtained in previous field trials (8). Where Cyanamid was washed into the soil immediately after application, the production of ammonia and nitrate nitrogen was rapid; after 8 days it was almost as high as that of the ammonium sulfate plot. The plot in which the Cyanamid was mixed with moist soil produced ammonia and nitrate less rapidly than did the plot that had been thoroughly sprinkled immediately after application of the fertilizer, but developed a much higher content of soluble nitrogen than did the plot on which the granules were applied to the surface and water was withheld for 2 weeks. At no time was a significant amount of urea, calcium cyanamide, or dicyandiamide found in any of the soils. The total nitrogen found in the soil and granules on the block receiving no water for 2 weeks after application of Cyanamid was somewhat lower, however, than the calculated theoretical amount, a result that suggested possible loss of ammonia to the atmosphere.

To measure any such possible loss from the granules, a 1-gm. sample of granular Cyanamid was moistened on a watch glass and covered by an inverted funnel. Air was pulled over the sample and aspirated through standard acid. An average of a number of trials indicated that under these laboratory conditions 1.5 mgm. of nitrogen as ammonia was lost per gram of Cyanamid in 24 hours. This is not a large loss, but if it continued in the field at this rate for 2 weeks it would amount to 21 mgm., or 10 per cent of the total 210 mgm. of nitrogen present in 1 gm. of Cyanamid.

The changes in composition of the granules are given in table 1. A white



crystalline coating gradually formed on the granules applied to moist soil and given no water for 2 weeks. These granules lost nearly half of their nitrogen in the first 4 days, as evidenced by the presence of only 12 per cent nitrogen at the end of that time. After this initial period, however, the rate of removal was slow, and when water eventually was applied the nitrogen was not removed rapidly.

Cyanamide nitrogen had virtually disappeared after 8 days from the granules receiving the heavy moisture applications, but significant quantities were still present in the dry coated granules after 28 days. Little dicyandiamide nitrogen was formed on the high-moisture plots, but as much as 6 per cent was found in the granules under the low-moisture conditions.

TABLE 1

*Percentages of nitrogen in Cyanamid granules at intervals after application to the surface of soil under different moisture treatments*

Original nitrogen content of Cyanamid, 21 per cent

FORM OF NITROGEN	MOISTURE TREATMENT	DAYS AFTER APPLICATION						
		4	8	12	16	20	24	28
Total nitrogen	Water withheld for 2 weeks after application of Cyanamid	12.0	11.4	10.0	10.2	7.5	6.9	6.1
	Sprinkled at 4-day intervals	12.0	10.5	8.6	5.7	5.2	5.4	6.1
	Soaked after application	5.4	3.2	1.3	1.1	0.7	...	...
Cyanamide nitrogen	Water withheld for 2 weeks after application of Cyanamid	11.8	8.5	5.5	5.5	5.5	5.0	3.5
	Sprinkled at 4-day intervals	11.8	6.0	5.5	5.0	4.5	4.5	2.0
	Soaked after application	4.9	1.5	0.5	0.5	0.5	...	...
Dicyandiamide nitrogen	Water withheld for 2 weeks after application of Cyanamid	Trace	3.0	4.0	2.0	2.5	2.0	2.5
	Sprinkled at 4-day intervals	Trace	3.5	2.0	0.5	0.5	1.0	3.1
	Soaked after application	Trace	0.5	0.2	0.5	0.2	...	...

The results obtained under the low-moisture treatments were compared with analyses of crystal-coated Cyanamid granules collected from beneath apple trees in the dry season of 1936. Figure 1 is a photomicrograph of these granules with part of the crust cracked off, showing the inner black granule of much the same appearance as when first applied. It was found that much of the outside crust on the granules was calcium carbonate (table 2). These granules retained a large part of their nitrogen until late summer under the dry conditions prevailing, and much of this nitrogen was in the form of dicyandiamide. The water-soluble calcium declined rapidly and was replaced by less soluble forms. It is significant that, for the inside of the granules 44 and 127 days after application, the percentage of carbonate, when expressed as calcium carbonate, is approximately the

same as when determinations were made for total calcium and the result expressed as calcium carbonate. This would indicate that all the calcium is changed to calcium carbonate when the granules are exposed on the soil under low-moisture conditions. The higher percentage of carbonate on the outside than in the inside of the granules 14 days after application suggests that the calcium moves to the outside, where it reacts with carbon dioxide of the air. Later, when all the calcium is changed to the carbonate, some may be lost by sloughing off from the outside, giving a greater percentage on the inside.

Further information on the reactions within Cyanamid granules was obtained from study of the fertilizer placed on the screen out of contact with the soil. Data given in table 3 show that these granules, which were not exposed to leaching, increased in weight by more than 20 per cent after 45 days of exposure.



FIG. 1. PHOTOMICROGRAPH ( $\times 15$ ) OF CYANAMID GRANULES COLLECTED 3 MONTHS AFTER BROADCAST APPLICATION TO APPLE TREES. NO RAIN FELL ON THE GRANULES FOR 2 WEEKS AFTER APPLICATION

Note formation of white crystalline crust on outside of original surface of granule

This was apparently due to the carbon dioxide taken up from the air. It is also significant that the total nitrogen in the sample decreased on continued exposure, although no moisture except that condensing from the air reached the granules. After 45 days' exposure the sample had lost over 14 per cent of its original nitrogen. It, like the granules taken from the orchard, showed formation of dicyandiamide nitrogen, decrease in soluble calcium, and increase in carbonates.

Analyses of both the inner and outer portions of these granules revealed that the formation of the white crust was the result of a deposition of a mixture of calcium carbonate, dicyandiamide, and other compounds. Close observation of these granules under binoculars showed this crust, in the process of formation, to be composed of needle-like transparent crystals (fig. 2) and a mixture of opaque white crystals, many of rhomboid form. Careful separations of the

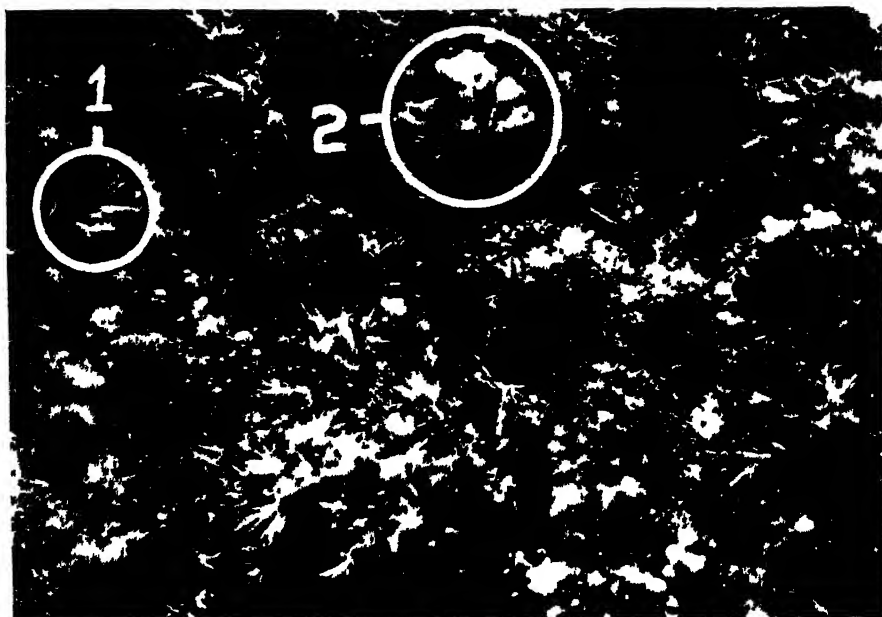


FIG. 2. PHOTOMICROGRAPH ( $\times 10$ ) SHOWING FORMATION OF CRUST ON CYANAMID GRANULES UNDER ALTERNATE WETTING AND DRYING IN THE PRESENCE OF CARBON DIOXIDE

Long needles —1— are calcium cyanamide; round pustules —2— are mixtures of calcium hydroxide, calcium carbonate, and dicyandiamide.



FIG. 3 PHOTOMICROGRAPH ( $\times 10$ ) OF CYANAMID GRANULES SHOWING CALCIUM CYANAMIDE NEEDLES MIXED WITH DICYANDIAMIDE AND CALCIUM CARBONATE

Crust developed in laboratory under alternate wetting and drying in presence of liberal

needle-like crystals disclosed that they were water-soluble, had a melting point of 43°C., and gave a positive qualitative test for the cyanamide ion. The rhom-

TABLE 2

*Chemical composition of Cyanamid granules collected from beneath apple trees in a season of low rainfall (1936)*

Results of analyses, in per cent

CHEMICAL CONSTITUENTS	PORTION OF GRANULES	DAYS AFTER APPLICATION				
		0	14	30	44	127
Total nitrogen.....	Entire	21.0	11.0	7.7	2.5	1.0
Cyanamide nitrogen.....	Entire	....	2.2	Trace	Trace	Trace
Dicyandiamide nitrogen.....	Entire	....	8.0	5.8	2.0	0.8
Water-soluble calcium as $\text{Ca}(\text{OH})_2$ .....	Entire	60.7	24.2	10.5	2.1	0.8
Total calcium as $\text{CaCO}_3$ .....	Entire	....	75.6	74.1	77.7	75.5
Carbonate as $\text{CaCO}_3$ .....	Outside	3.1	42.0	32.9	36.9	34.5
	Inside	3.1	30.0	46.8	77.2	78.8
Calcium as $\text{CaCO}_3$ .....	Outside	....	46.6	52.8	46.6	60.0
	Inside	....	75.5	73.7	76.2	78.4

TABLE 3

*Changes in Cyanamid granules placed on a screen and exposed to atmospheric moisture but protected from rain*

	DAYS AFTER APPLICATION			
	0	10	24	45
Weight of sample.....gm.	50.0	54.0	57.6	60.3
Total nitrogen in sample.....gm.	10.5	10.5	10.2	9.0
Cyanamide nitrogen.....per cent	0	18.5	13.5	6.0
Dicyandiamide nitrogen.....per cent	0	0.5	2.5	7.0
Water-soluble calcium as $\text{Ca}(\text{OH})_2$ .....per cent	60.7	34.0	21.8	16.2
Carbonate as $\text{CaCO}_3$ .....per cent	3.1	6.2	32.0	58.6

TABLE 4

*Chemical composition of inner and outer portion of Cyanamid granules after 24 days' exposure to atmospheric moisture but protected from rain*

Results of analyses, in per cent

CHEMICAL CONSTITUENTS	INSIDE	OUTSIDE	TOTAL
Cyanamide nitrogen.....	17.5	12.0	13.5
Dicyandiamide nitrogen.....	.5	4.0	2.5
Soluble calcium as $\text{Ca}(\text{OH})_2$ .....	18.7	24.6	21.8
Carbonate as $\text{CaCO}_3$ .....	25.0	40.6	32.0
Calcium as $\text{CaCO}_3$ .....	80.9	81.2	78.9

boid crystals were insoluble in water and soluble in dilute acid, indicating they were those of calcium carbonate.

On Cyanamid granules treated in a closed chamber with alternate atmospheres of moist carbon dioxide and moisture-free air, it was possible to observe the rapid formation of this crust. Figure 3 shows the start of the formation; close observation reveals the needle-like crystals of cyanamide protruding from the crust. When the air passed over the granules contained no carbon dioxide, the crust was very slow in forming.

#### SUMMARY AND CONCLUSIONS

Cyanamid granules applied broadcast to the surface of soil in periods of dry weather became coated with a white crust. When the granules were exposed to soil moisture but protected from precipitation, more than one-third of the nitrogen was changed to dicyandiamide or was lost to the air as ammonia in 8 days. Precipitation soon after the fertilizer application leached most of the nitrogen into the soil. Observations and analyses of the inside of the granules and of the white crust showed that the calcium hydroxide formed was all changed to calcium carbonate and much of the nitrogen to dicyandiamide in the outer white crust. These two compounds produced an insoluble coating, which prevented the rapid removal of the nitrogen from the inside of the granule when rains did fall.

These results point to the necessity of broadcasting granular Cyanamid during periods of rainy weather to obtain the best results. Where it must be applied under dry weather, it should be worked into the soil. Even in periods of high rainfall the results probably will be more satisfactory if it can be cultivated into the soil.

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# POTASSIUM RETENTION FROM ANNUAL ADDITIONS OF CHLORIDE, SULFATE, AND NITRATE, AS INFLUENCED BY LIMESTONE AND BY DOLOMITE

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The potassium content of commercial fertilizers is supplied chiefly as either the chloride or the sulfate. These two salts are used distinctively for certain plants, primarily because of the supposed differential effects of the Cl and SO<sub>4</sub> ions upon the quality of the resultant crops. It has not been shown, however, that the several phenomena of retention, fixation, liberative effect, and outgo of potassium are respectively identical for additions of potassium in variant anion combination. Moreover, it is not known whether the conservation of the potassium supplied by the manurial salts is affected to the same extent by chemically equivalent incorporations of calcic and dolomitic limestones.

This paper gives the results of a 10-year lysimeter study of the influence of anion combination upon the *retention*<sup>1</sup> of potassium from equivalent quantities of chloride, sulfate, and nitrate as annual surface applications to three fallow soils, with and without single full-depth incorporations of calcic limestone and of dolomite. Corollary objectives were to determine whether retention of potassium is proportionate to rate of application and to integrate such retention with the attendant conservation of the calcium and the magnesium introduced by the two types of limestone. The study was restricted to the conservation of the several bases within the zone that received the surface applications and the full-depth incorporations.

## EXPERIMENTAL PROCEDURE

### *Soils used*

The three soils used were distinctly different in type, origin, and characteristics. Pertinent analytical data are given in table 1. Hartsells fine sandy loam was derived from the sandstone formation of the Cumberland Plateau and was decidedly acidic. The more fertile Cumberland silt loam was derived from Knox dolomite and also was acidic. Calhoun silt loam was of loessal origin and was slightly alkaline, with an ammonium acetate determination of exchange capacity less than that of either of the two acidic soils. The soils differed decidedly also in the ratios of their exchangeable calcium and magnesium contents, and the exchangeable potassium content of the alkaline Calhoun soil was only about one third that of the two acidic soils.

<sup>1</sup> The term *retention* is used to connote the quantity of potassium not recovered in the rainwater leachings from the surface applications of the three potassic salts. Those fractions of additive potassium that underwent chemical fixation and "mineralization" and any that remained in the forms applied are to be determined by a laboratory study of the soils reserved at the end of the 10-year period.

*Soil placement*

The total quantity of each soil used was obtained from a level representative area and then sifted and mixed under shelter to assure uniformity. The placement in every 1/20,000-acre lysimeter was approximately 7 inches in depth, and was the equivalent of 100 pounds of moisture-free soil. Each column of soil rested on a bed of quartz, and leachate compositions therefore were not subject to the alterative effect of an underlying stratum of subsoil.

TABLE 1

*Calcium carbonate content, pH, and exchangeable base content of soils in lysimeter experiment*

SOIL		CaCO <sub>3</sub> CONTENT*		REACTION†		EXCHANGEABLE BASE CONTENT									
						Milligram equivalents per 100 gm.				Pounds CaCO <sub>3</sub> ∞ per 2,000,000 pounds					
										Exchange capacity‡	Ca	Mg	K§	H	Exchange capacity‡
Number	Type	Initial	Final	Initial	Final	per cent	per cent	pH	pH						
6348	Hartsells fine sandy loam	.025	.025	5.07	5.00	9.5	1.7	0.9	0.37	6.53	9500	1700	900	370	6530
6349	Cumberland silt loam	.018	.014	5.61	5.10	7.9	2.6	0.4	0.35	4.55	7900	2600	400	350	4550
6347	Calhoun silt loam	.132	.057	7.40	7.00	5.2	6.7	0.6	0.13	0	5200	6700** (4470)††	600	130	0

\* By unpublished titrametric modification of the tentative method (1, p. 3).

† By glass electrode.

‡ By ammonium acetate.

§ By gravimetric cobaltinitrite procedure of Wilcox (17).

|| By difference between total exchange capacity and the combined Ca, Mg, and K values.

\*\* Not corrected for CaCO<sub>3</sub> content dissolved by the ammonium acetate.

†† By difference between total exchange capacity and the combined Mg, K, and H values.

*Soil treatment*

The annual applications of the three potassic salts were made in solution to assure even distribution over the surface areas. The total input of each salt for the 10-year period amounted to 2,094 pounds of K<sub>2</sub>O per 2,000,000 pounds of soil. The initial applications were at the 200-pound rate; those made at the beginning of every subsequent annual period were at the 210.4-pound rate. In a companion series, the Cumberland soil also received corresponding annual applications of potassium sulfate at a fourfold rate until eight additions had provided a 6,691-pound input of K<sub>2</sub>O. Since outgo of potassium therefrom then had become about equal to the input, the fourfold additions were discontinued.

The limestone was an Appalachian marble of 99 per cent CaCO<sub>3</sub> content. The dolomite was from the Knox formation and contained 51 per cent of CaCO<sub>3</sub> and

37 per cent of  $\text{MgCO}_3$ . Both materials were finer than 100 mesh. The single incorporation of limestone, and of dolomite, was made in full depth and corresponded to a rate of 1 ton of  $\text{CaO}$ , or 3,570 pounds of  $\text{CaCO}_3$ , per 2,000,000 pounds of soil. These incorporations were made just prior to the first of the 10 annual surface applications of the potassic salts, and thereafter the soils in the 36 lysimeters were maintained fallow and were undisturbed.

### *Analytical technic*

During the first 6 years of the experiment the rapidity of outgo of potassium and the extent of its retention were determined through the analysis of each of the 28 successive periodic collections of leachates from the 36 lysimeters. Yearly retention of potassium thereafter was computed from the analysis of every composite of the several periodic collections of each annual period. The analytical separation of potassium was effected by means of the well-known platonic chloride method. Concomitant outgo of calcium and magnesium was determined also by the use of the conventional method in the analysis of each annual composite of leachates, but this outgo will be referred to only as it may serve to explain differences in retention.

### RETENTION OF POTASSIUM

Amounts of potassium retained against the leaching action of a mean annual rainfall of 51 inches are expressed in terms of pounds of  $\text{K}_2\text{O}$  per acre of 2,000,000 pounds, and as percentages of the amounts added. The mean of losses from the no-treatment controls was subtracted from the outgo from the soil that received only a potassium salt, and this value was then subtracted from the amount of the  $\text{K}_2\text{O}$  addition. The retentive effects of the liming materials were computed by a corresponding usage of the soils that received potassic salts alone as controls against those that received both a potassic salt and either limestone or dolomite. The determined cumulative retentions are graphed against absolute retentions in figures 1, 2, and 3.

*Hartsells fine sandy loam.* Potassium retention from the sulfate invariably was less than the retention from the chloride or the nitrate in the acidic soil, in the one limed, and in the one dolomited. The retentions from the chloride and nitrate were so nearly identical as to warrant the use of their mean values in comparisons with the retentions from the sulfate. The mean overall K-retention from the chloride and nitrate additions was 1,035 pounds, or 49.4 per cent for the unlimed soil, whereas that from the equivalent sulfate additions was 44.6 per cent. These values are from significant analytical differences. They indicate that a larger fraction of the sulfate was leached unchanged and that the replacements of Ca and Mg by the K of the salts of the monovalent acids exceeded the replacements induced by the K of the sulfate. The most pronounced retention of additive potassium by the decidedly acidic unlimed fine sandy loam occurred in the initial 3-year period, during which the mean of the per annum retention from the three salts was 82 per cent of the annual input.

Both limestone and dolomite increased the total retention of potassium from



each of the added salts. Similar results as to the repressive effects that various calcic, magnesian, and dolomitic materials exert upon the solubility of soil potassium, as registered by the incidence of potassium in the free soil water, have been presented in a series of papers (2, 3, 8, 9, 11, 12, 13, 14, 15, 16). The single instance of the opposite effect was the enrichment in potassium content of drainage waters through hydrolysis of native supplies of potassium as an initial and transient effect induced by excessive incorporations of ground burnt lime, or CaO (2).

Although both limestone and dolomite increased the retention of potassium until the tenth year, this effect was more pronounced during the first 3 years. The mean of the first three annual retentions of potassium by the Hartsells soil with limestone and dolomite supplements was 87 per cent of the annual addition. The decidedly decreased annual retentions of potassium from the unlimed soil, from the limested soil, and from that dolomited, did not appear until the seventh year.

The leachates were derived solely from rainfall, the periodicity of which was such that seldom, if ever, were the lysimeter soils subjected to a rigorous leaching, or "flushing," comparable to that of a laboratory aqueous extraction. With no surface runoff, about 45 per cent of the 51-inch annual rainfall passes through the soil. The higher percentage retentions of potassium during the first 3 years cannot be attributed, however, to sluggishness of gravitational movement of the potassium solutes through the column of soil and to retentions of the additive salts as such, since the companion analyses of the periodic collections during the initial 3-year period established the complete recovery of the input of the associated Cl and SO<sub>4</sub> from the limested and dolomited soils, wherein maximal retention of additive potassium had occurred. Moreover, it was during this period that maximal enhancement of Ca and Mg outgo occurred. This phenomenon reflects the substantial build-up of added potassium into potassic complexes and the progressive diminution in the supplies of calcium and magnesium in the complexes formed by the added liming materials. The greater retention of K and the maximal outgo of Ca and Mg during the initial year is attributed to both the hydrolytic dissolution of the generated alkaline-earth complexes and the replacement of their Ca and Mg content by the added potassium.

The fact that dolomite was somewhat less potent than limestone in the retention of potassium from the several potassic additions is integrated with the greater mobility of the magnesium salts generated from the more readily hydrolyzable magnesium complexes derived from the incorporated dolomite. The decomposition of incorporated dolomite usually caused substantial enhancement in the magnesium content of the rainwater leachings from soil of appreciable exchangeable calcium content, without concomitant enrichment of calcium content.

The graphs of figure 1 show the cumulative retentions of potassium by the Hartsells soil, as the respective means of the separate values for the three potassic salts, alone, with limestone, and with dolomite, in relation to absolute retention. The curve for the mean retention of the three salts by the unlimed Hartsells soil shows an approximate retention of 500 pounds of K<sub>2</sub>O from the 620.8-pound input during the first 3 years. The curves emphasize the magnitude of the

K-retention induced by the two limestones during the initial 3-year period and show the persistence of their effect upon such retention. They show also that the retentions induced by the originally equivalent quantities of the two limestones were of like extent during the first 6 years and that, thereafter, the greater retention of K induced by the conserved supply of exchangeable calcium and the diminished supply of exchangeable magnesium derived from the incorporated dolomite was less than the K-retention induced by the larger residues of calcium from the incorporated limestone.

At the conclusion of the experiment there were no carbonates residual from the limestone and dolomite incorporations. Complete disintegration of the incorporations of the two types of limestone undoubtedly had occurred before the second addition of the potassic salts. This conclusion is warranted by the

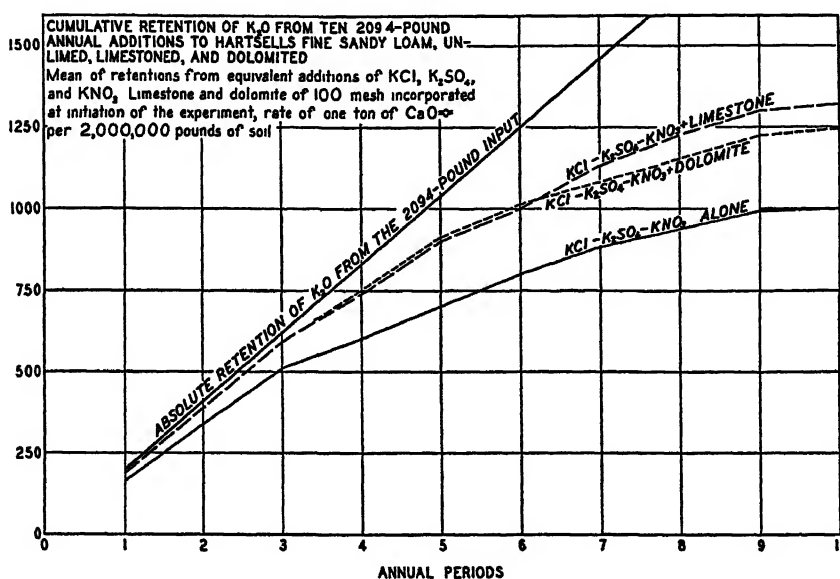


FIG. 1

findings of related investigations (6, 10), by similar unpublished studies, and also by the determinations of every yearly outgo of calcium and magnesium throughout the present experiment. The definite effects that both types of limestone exerted upon retention of potassium continued, however, long after the decomposition of the limestones and, therefore, were due chiefly to the hydrolysis of the alkaline earth complexes that had been generated by the added calcium and magnesium, rather than to the direct dissolution of the limestones.

*Cumberland silt loam.* In general, the foregoing observations as to the effects induced by the 2,094-pound 10-year input of  $K_2O$  in the Hartsells soil apply also to the effects induced by the same additions to the less acidic Cumberland silt loam. The magnitude of K-retention by the Cumberland soil was, however, decidedly less than that by the Hartsells soil. The mean of the nine overall retentions from the total  $K_2O$  input of 2,094 pounds to this silt loam was 44.7 per

cent against a corresponding mean of 57 per cent for the nine overall retentions by the Hartsells fine sandy loam.

Again, in every group, the least 10-year retention of potassium from the 2,094-pound  $K_2O$  additions was that from the potassium sulfate. The mean retention of potassium from the six chloride and nitrate treatments was 58.7 per cent, whereas the mean from the three sulfate treatments was only 53.7 per cent. Attainment of a near-balance between input and outgo of potassium for the Cumberland soil after 9 years was similar to such attainment for the Hartsells soil.

The three lower curves of figure 2 were constructed by the use of combinations of the respective means for  $KCl$ ,  $KNO_3$ , and  $K_2SO_4$ . They show the cumulative retentions of  $K_2O$  from the 2,094-pound 10-year input to Cumberland silt loam,

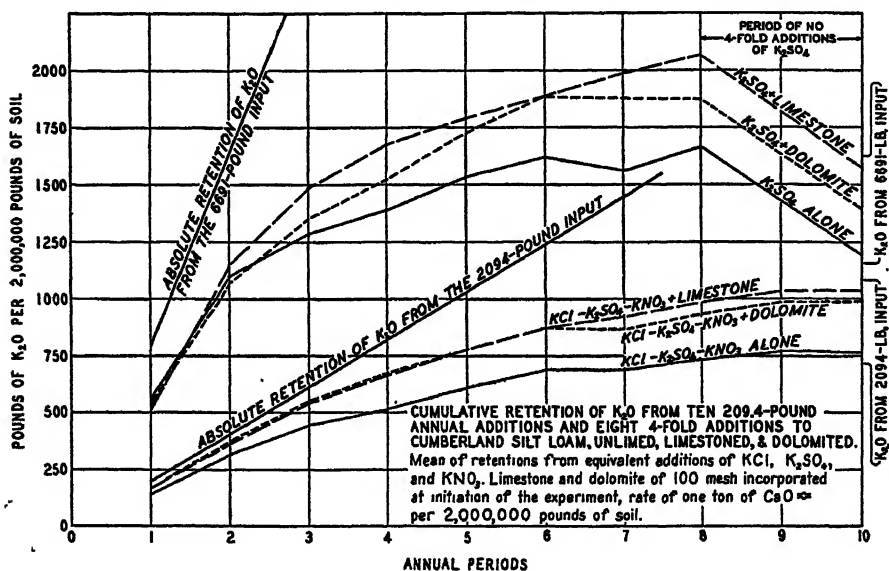


FIG. 2

with and without liming, in relation to complete retention. The greater retentions by the limed and dolomited soils are obvious. As in the Hartsells soil, limestone and dolomite varied in repression of potassium outgo only after 6 years, and the overall retention induced by the limestone was somewhat greater than that induced by the dolomite.

Companion applications of potassium sulfate totaling 6,691 pounds of  $K_2O$  were made to Cumberland silt loam at the mean rate of 836.4 pounds per annum, alone, and with limestone and with dolomite only. Since the recovery of potassium during the seventh year had been found to approximate the annual input, the fourfold treatments were discontinued after the eighth annual additions, which were made before the composited leachings of the seventh year had been analyzed.

Mean annual retentions of 535 pounds and 531 pounds of  $K_2O$  from the several

fourfold additions of potassium sulfate took place during the first and second years. This was equivalent to 38 per cent of the mean of the overall retentions from the annual additions during the first 8 years of the 10-year period. Considerable actual and percentage recoveries of  $K_2O$  from the heavy additions of  $K_2SO_4$  occurred even during the first year, whereas similar proportionate recoveries from the several 209.4-pound annual additions of the three potassic salts, particularly those made to limed soils, did not come until the fourth year. The 10-year retentions from the 8-year input of 6,691 pounds of  $K_2O$  as the sulfate, alone, with limestone, and with dolomite were 1.8, 1.6, and 1.5 times the respectively corresponding retentions from the input of 2,094 pounds of  $K_2O$  through 10 annual additions. The mean retention of  $K_2O$  from all of the fourfold  $K_2SO_4$  applications during the first 8 years of the 10-year period was 140 pounds, whereas the mean annual retention from the 10 annual sulfate additions of  $K_2O$  at the 209.4-pound rate was 86 pounds.

The cumulative retentions of  $K_2O$  from the fourfold sulfate additions are graphed against absolute retention in figure 2. The curves for the limed and dolomited soils show an overall similarity as to the effect of liming upon retention of the added potassium. The effect of the calcic limestone, however, was the more pronounced after the second year. Since the outgo of  $K_2O$  during the ninth and tenth years constituted a draft upon the 8-year accumulations, the overall retentions for the 10-year period was less than the 8-year retentions for both unlimed and limed soils.

The mean of the  $K_2O$  totals leached from the 6,691-pound applications was 4.6 times the mean for the totals leached from the 2,094-pound  $K_2O$  input. The percentage recoveries from the fourfold potassium sulfate additions to the unlimed, limed, and dolomited soils were 82, 76, and 79, respectively, for the 10-year period, and the applied sulfate passed through the soil chiefly in that form. This was evident from the determined outgo of Ca and Mg from the supplies native to the soil and that derived from the limestone and dolomite incorporates. As noted, the eighth annual additions of potassium sulfate at the fourfold rate were made before the outgo of potassium for the seventh annual period had been determined. Each build-up of K-complexes that occurred during those 7 years, supplemented by the eighth application, therefore, was subjected to a 3-year period of leaching after the soil had ceased to retain additive potassium. During the last 2 years, wherein no potassium sulfate was added, the potassium leachings from the several accumulations from the eight previous applications at the fourfold rate were substantially identical for the acidic soil, that limed, and that dolomited. The amounts of  $K_2O$  then leached per annum, however, were only about a third of those leached annually during the 3-8-year period. Nevertheless, the outgo of  $K_2O$  from the 6,691-pound addition to the unlimed Cymberland silt loam was 3.8 times the outgo from the 2,094-pound addition, although the full input by the eight heavy additions was only 3.2 times the 2,094-pound input through the 10 annual additions.

Although the companion determinations of annual outgo of calcium and magnesium are not reported, it should be noted that the releases of the potassium

from stores that had been accumulated from the eight annual additions induced substantial repressions in the outgo of calcium and magnesium from both native and acquired supplies of those two elements. During the last 2 years the annual leachings of calcium and magnesium, concomitant with the outgo of potassium from the previous heavy input of  $K_2SO_4$ , were only a third as much as the annual leachings of those two elements from the continued 209.4-pound mean annual input of  $K_2O$ , alone, with limestone, and with dolomite. Furthermore, the mean of those concomitant leachings of calcium and magnesium amounted to only 43 per cent of the calcium and magnesium leached from the *untreated* soil. Thus, after the additions of  $K_2SO_4$  at the fourfold rate had been discontinued on the unlimed Cumberland soil, on that limed, and on that dolomited, when those soils had ceased to retain additive potassium, the accumulated K-complexes registered a decided increase in K-hydrolysis. This K-hydrolysis repressed and far exceeded the hydrolysis of the calcic and magnesian complexes, those native to the soil, and also those resultant from the incorporated limestone and dolomite. In contrast, the ninth and tenth applications of  $K_2SO_4$  at the lighter rate resulted in a continued enhancement in the outgo of calcium and magnesium far beyond the outgo of those two elements from the untreated soil and in keeping with the enhancements induced by the lighter additions of  $K_2SO_4$  during the fourth to eighth annual periods. This reversal, however, did not offset the earlier increases in retention that had been induced by the two liming materials. The terminus of the retention curve for dolomite is well above the terminus of the curve for the unlimed soil and the terminus of the curve for limestone is still higher. As in the previous comparisons, in time the limestone was more effective than dolomite in causing retention of additive potassium.

*Calhoun silt loam.* Although its inherent reaction is mildly alkaline because of its 0.132 per cent  $CaCO_3$  content, this soil is not calcareous, in the usual connotation of that term. Its meager content of exchangeable potassium was reflected by the fact that the mean of the losses of potassium from the untreated controls was less than a third of the losses of potassium from the one of untreated acidic soils, and less than one half of that from the other.

The retention of the additive potassium by the naturally alkaline soil was virtually a constant for the three anion combinations. The most pronounced retention occurred during the first 3 years, after which there was a decided diminution in the amount retained from every annual addition. The cumulative retentions are graphed to absolute retention in figure 3. The curves for the effects of limestone and dolomite are almost identical. The mean of the 10-year retentions of  $K_2O$  by the unlimed Calhoun soil was 907 pounds, or 43 per cent of the total input. This retention was intermediate between the overall retentions of 1,001 pounds and 787 pounds by the Hartsells and Cumberland soils, respectively.

Since this silt loam contained no measurable quantity of exchangeable hydrogen, the moderate incorporations of limestone and of dolomite did not alter its reaction appreciably. Moreover, the pH values and the carbonate analyses of

table 1 confirm the previous findings (14) that no-treatment controls of the Calhoun soil did not become acidic as the result of 10 years of rain-water leachings. In contrast to the marked effect induced by limestone and by dolomite on the two initially acidic soils, the effect of these two limings upon potassium retention by the initially alkaline Calhoun soil was virtually nil during the first 3 years and only slight for the 10-year period.

The slightly alkaline Calhoun silt loam likewise registered maximal retention of additive potassium during the initial 3-year period and near-saturation therewith during the tenth year. Its overall K-retention was not affected appreciably, however, by either anion combination or type of incorporated limestone. The mean of the retentions of K by the unlimed Calhoun soil of relatively high ex-

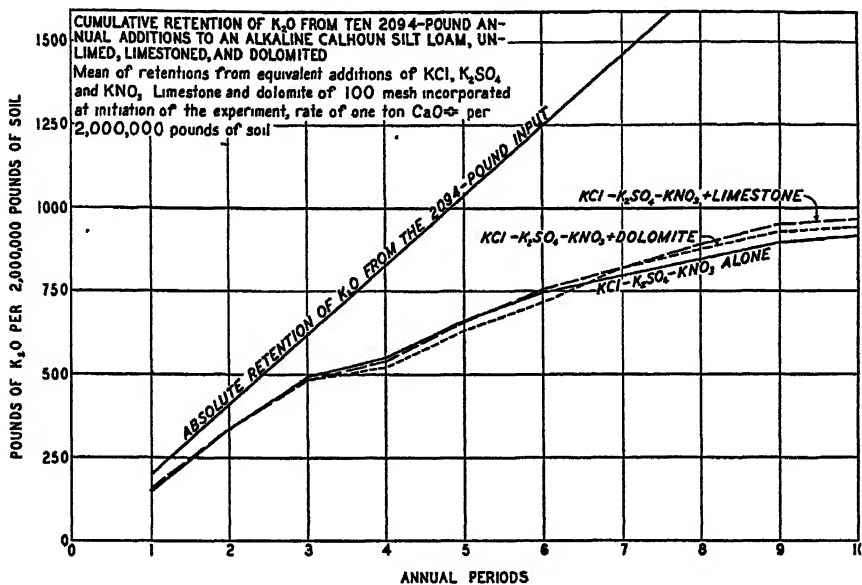


FIG. 3

changeable Ca content exceeded that exerted by the acidic Cumberland loam, but was less than that exerted by the strongly acidic Hartsells soil.

Retentions of K from the equivalent additions of the three potassic salts invariably induced exchange reactions and increased outgo of calcium and magnesium until the tenth year.

The potentiality of the additive potassium to effect replacement of calcium and magnesium did not overcome the effect of the single moderate incorporation of limestone to increase retention of potassium or to repress the outgo of magnesium from supplies native to the soil.

The effects of a 2,094-pound input of  $K_2O$  to Cumberland silt loam through 10 annual applications of  $K_2SO_4$  were integrated with the effects induced by an input of 6,691 pounds through eight annual applications of the sulfate. The mean of the total retentions in the nine Cumberland soil units that received  $K_2O$  at the

lesser rate was 934 pounds; the corresponding mean for the three applications at the fourfold rate was 1,396 pounds. The mean effect of limestone and dolomite was a 271-pound increase in the total retention of  $K_2O$  from the 2,094-pound input and a 291-pound increase in the total retention from the 6,691-pound input. As long as the fourfold annual additions of potassium sulfate were made to the Cumberland soil—unlimed, limested, and dolomited—there was an increase in the outgo of Ca and Mg. After the additions were discontinued, however, the hydrolysis of the built-up supply of K-complexes repressed the hydrolysis and outgo of the Ca and Mg from the complexes derived from the limestone and the dolomite to the unprecedented level of less than half of the Ca + Mg outgo from the untreated soil.

#### SUMMARY

Three typical Tennessee soils—an acidic Hartsells fine sandy loam, an acidic Cumberland silt loam, and a slightly alkaline Calhoun silt loam—each unlimed, limested, and dolomited, were used in a 10-year lysimeter study of the influence of anion combination upon K-retention from annual surface applications of dissolved chloride, nitrate, and sulfate. Total input of  $K_2O$  by each potassic salt was 2,904 pounds. The single incorporations of 100-mesh limestone and of dolomite were made full depth at the per-acre rate of 1 ton of  $CaO$ , or 3,570 pounds of  $CaCO_3$ , immediately before the initial applications of the three potassic salts.

The 1,152 determinations of the potassium content of 49 collections of rain-water leachings were utilized to compute the respective differences between the amounts of  $K_2O$  added and those retained during a 10-year period.

The maximal annual retention of potassium from the mean annual input of 209.4 pounds of  $K_2O$  by any potassic salt was 97.3 per cent. The largest percentage retentions occurred in all soils during the initial 3-year period. In 12 of 27 units, the retention of potassium from the 209.4 mean annual input of  $K_2O$  was virtually nil during the tenth year.

Percentage retention of K by the acidic Hartsells fine sandy loam, and also that by Cumberland silt loam, were virtually identical for the applications of chloride and nitrate, but invariably were less for the sulfate applications. The K-retentions from the three salts applied to these two soils were increased by both limestone and dolomite, the effect of the limestone being the more pronounced. The respective means for 10-year retentions of  $K_2O$  by the two unlimed, the two dolomited, and the two limested soils were 42, 54, and 57 per cent, respectively, for the common 2,094-pound input.

Additional overall effects from the 6,691-pound input of  $K_2O$  were (a) no increase in the outgo of calcium derived from the limestone or from the dolomite, (b) small decreases in the outgo of magnesium from the limested soil and from the magnesium supplied by the dolomite, (c) substantial percentage increase in the Ca + Mg from the unlimed soil, and (d) decreases in the Ca + Mg derivative from the limestone and from the dolomite.

## CONCLUSIONS

The retention of potassium to be expected from surface applications of  $K_2SO_4$  to the Hartsells and Cumberland soils would be significantly less than for equivalent quantities of the chloride and the nitrate. The larger the addition of potassium salt, the greater will be the total losses of K and those leached in the form applied. Retentions by the alkaline Calhoun soil would be virtually identical for the three salts and not affected appreciably by either limestone or dolomite.

Since the potassium retentions from the 209.4-pound annual applications of the three potassium salts to the three soils were (a) invariably greater although not absolute during the initial 3-year period and the subsequent retentions were decreased substantially, and (b) about 80 per cent of the initial application of 800 pounds of  $K_2O$  was lost, it appears that a rapid build-up of K-complexes by heavy additions of potassic salts to these soils would not be either feasible or economic.

Since continued applications of potassic salts deplete the calcium and magnesium content of acidic soils, it is obvious that this depletion should be offset by adequate liming. Conversely, however, incorporations of limestone and of dolomite tend to decrease the solubility of both native and additive potassium *within the zone of their incorporation* and thus affect the supply of nutritional potassium. This reciprocal relationship should be recognized to assure a proper balance of Ca, Mg, and K in a rational liming and fertilizer program.

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# THE TREND OF PHOSPHATE ADSORPTION BY INORGANIC COLLOIDS FROM CERTAIN INDIANA SOILS<sup>1</sup>

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That soils "fix" or retain applied soluble phosphate in more or less difficultly available forms has long been known. Because of the overlapping effect of the many forces involved in this process, however, it is difficult to evaluate each one properly and independently in a system as complex as the soil. As pointed out by Murphy (15) "the term *phosphate fixation* carries no implication of the mechanism by which removal takes place or of the nature of the products formed."

The extensive literature on phosphate fixation indicates two general types of reactions, i.e., fixation by *precipitation* and by *adsorption*. Precipitation of phosphates by Ca, chiefly as the tricalcium salt, occurs in soils when the reaction exceeds pH 6.0 (4, 8, 19, 21). The formation of high-calcium salts such as carbonato-apatite [ $3 \text{ Ca}_3(\text{PO}_4)_2 \cdot \text{CaCO}_3$ ] and hydroxy-apatite [ $3 \text{ Ca}_3(\text{PO}_4)_2 \cdot \text{Ca}(\text{OH})_2$ ], as reported by McGeorge *et al.* (11), is regarded as a contributing factor to low phosphate availability in calcareous alkaline soils.

The early literature is rich in references to the precipitation of phosphates by Fe and Al ions in acid soils with the implication that these ions are largely responsible for fixation. Except in strongly acid soils, the quantity of ionic Fe and Al is probably too low to account for any considerable precipitation of phosphate (15). The more recent work of Ford (7), Heck (9) and Dean (6) has focused attention on the adsorption of phosphate anions by hydrated oxides (hydrogels) of iron, and to some extent of aluminum. Heck (9) suggested the adsorption of phosphate by the mineral goethite according to the following reaction:  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O} + \text{H}_3\text{PO}_4 = \text{Fe}_2(\text{OH})_3\text{PO}_4$  (dufrenite) +  $\text{H}_2\text{O}$ . Because artificially prepared Fe and Al hydrogels have been shown to adsorb phosphate anions tenaciously (10, 21), the natural soil hydrogels of these elements are considered to be more important in rendering phosphates unavailable by adsorption than are the ions of Fe and Al by precipitation.

Within the last decade the role of aluminosilicate colloids (clay minerals) in rendering phosphates insoluble has received considerable attention. Scarseth

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(17) found that montmorillonite adsorbed phosphate anions in significant quantities within the pH range of 5.0 to 7.0 with a maximum adsorption at pH 6.0. Stout (18) observed that kaolinite and halloysite adsorbed exceedingly large amounts of phosphate at pH 3.0 to 4.0 with a progressive decrease in this property with increase in pH. Scarseth (17) and also Ravikovitch (16) have reported the retention of phosphate by exchangeable Ca by a phenomenon subsequently referred to by Mattson and Karlsson (13) as "saloid-bound."

The study reported herein was undertaken to obtain detailed information on the trend of phosphate adsorption over a wide range of pH by the inorganic colloids in certain Indiana soils of varying maturity. Attention was also given, for studies of this nature, to the merits of the practice of removal of free iron oxide from soil colloids, a practice for which Toth (20) has suggested the term "deferration." The details on this phase of the present study are reported in a previous paper (1).

#### MATERIALS AND METHODS

##### *Selection and description of soils*

The inorganic colloids used in this study were obtained from the upper section of the B<sub>2</sub> horizon of three extensively developed soil types in Indiana—Miami, Cincinnati, and Frederick silt loams—which represent widely divergent soil conditions as to origin and composition. Material from this horizon, rather than surface material, was selected in order to provide a colloid fraction relatively free from humus.

Miami and Cincinnati silt loams are representative of soils having a common origin but differing in age or in stage of maturity. Both are developed from calcareous glacial till, the former of Late Wisconsin age (leached 40 inches) and the latter of Illinoian age (leached 12 feet). Frederick silt loam is residual from cherty limestone and is the oldest soil in this group. It is extensively developed in the limestone region in southern Indiana. All of these soils are light-colored and they occur on moderately sloping land having good external and internal drainage. A brief description of the B horizon of each follows:<sup>3</sup>

*Miami silt loam—B horizon* (14-30 inches). Light reddish-brown plastic heavy silty clay loam having a well-defined medium-nut angular structure. A few hard pebbles were present. Strongly acid in reaction. (Sampled in a road cut 2 miles northwest of Lafayette, Tippecanoe County, Indiana.)

*Cincinnati silt loam—B horizon* (18-32 inches). Light yellowish brown, medium plastic, silty clay loam which breaks naturally into lumps 1 to 2 inches in diameter having good angularity. No pebbles occur in this horizon. Strongly acid in reaction. (Sampled on Route 43 in a road cut 7 miles south of Greencastle, Putnam County, Indiana.)

*Frederick silt loam—B horizon* (18-36 inches). Yellowish-brown silty clay loam with brown coatings on the particle surface. The material breaks up into large angular particles 1 to 2 inches in diameter. Some chert fragments present. Strongly acid in reaction. (Sampled in a road cut 8 miles south of Salem, Washington County, Indiana.)

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<sup>3</sup> For a complete description of these soils, see Indiana Soil Survey Reports for Miami, Putnam, and Washington Counties, respectively.

### *Preparation of colloids*

In order to facilitate the separation of the inorganic colloid, a series of 100-gm. portions of the soil material were leached on 4-inch Büchner funnels with *N* NaCl until Na-saturated. After the excess electrolyte was removed by washing with distilled water, the Na-saturated material (about 1,000 gm.) was suspended by aid of a Bouyoucos deflocculator and poured into 5-gallon bottles for sedimentation. After settling for 4 days the top 28 cm. of suspension was siphoned off into another bottle of similar size. Special precaution was taken to prevent upward movement of particles larger than  $1\ \mu$  from below the 28-cm. mark. This was accomplished by progressively moving the siphoning pipette downward just in advance of the lowering liquid surface as the suspension was withdrawn. More water was added to the residue of the original sample, after which it was thoroughly agitated and the sedimentation process repeated at least twice, or until most of the colloid was recovered. This process removed a colloidal clay fraction having particles well under  $1\ \mu$  in effective diameter, subsequently referred to as *colloid*.

The colloidal suspensions from each soil were concentrated by use of clay filter candles and suction and were electrodialed to remove all mobile ions.

### *Phosphate adsorption technique*

The reaction is a governing factor in the retention of phosphate and certain other anions by soil colloids (12, 17). It is important, therefore, that the pH be accurately known for each independent colloid-phosphate system at equilibrium, on which the phosphate adsorbed is to be determined. If the procedure allows a shift in the reaction of the system during sampling, the colloid-phosphate equilibrium is upset and the analysis fails to reflect the true magnitude of adsorption. Some investigators dealing with phosphate fixation problems apparently have not taken this fact fully into account. During the present investigation the technic followed was essentially that described by Scarseth (17), which is designed to provide extracts for analysis by means of the centrifuge without disturbance of the equilibrium pH of the system being sampled.

The electrodialed Miami, Cincinnati, and Frederick colloids were diluted to contain exactly 2 gm. of material in 100 ml. of suspension. Fifty-milliliter portions of these suspensions were pipetted into each of a series of ten 250-ml. Erlenmeyer flasks, giving 1 gm. of colloid per flask. To each flask in the series distilled water and standard 0.1 *N* NaOH, or 0.042 *N* Ca(OH)<sub>2</sub>, were added in the order indicated, the amount of base being varied from flask to flask to provide different pH values over the range of 3.0 to 8.0. In all cases the sum of the water and base added to the colloidal suspensions equalled exactly 45 ml. This was followed after 1 hour by a final addition of 5 ml. of a standard solution containing 29.4 mgm. of H<sub>3</sub>PO<sub>4</sub>. These several additions resulted in a final volume of exactly 100 ml. containing H<sub>3</sub>PO<sub>4</sub> at the rate of 30 millimoles per 100 gm. of colloid. All additions of base and acid to the colloid were made while the latter was in vigorous motion. In order to supply 15- and 5-millimole concentrations

of  $\text{H}_3\text{PO}_4$  per 100 gm. of colloid the standard solution was diluted, 1 + 1 and 1 + 5, respectively, and used as previously indicated.

The flasks in the series for each adsorption experiment were kept at approximately 24–26° C. and shaken with a vigorous rotational motion three times daily for 5 days. Clear extracts of the colloid suspensions were obtained for analysis by pipetting 25 ml. into centrifuge tubes and adding 25 ml. of a 0.5 *N* phosphate-free NaCl solution, followed by centrifuging in an angle-head (Sorvall) centrifuge. Immediately after withdrawal of aliquots for centrifuging, the pH of each suspension in the series was determined with a Beckman pH electrometer.

### *Methods of chemical analyses*

The analyses of the colloids were made by official methods (2) and are reported in table 1. This table also includes the data for free iron oxides removed from the colloids by the biological deferration procedure of Allison and Scarseth (1),

TABLE 1  
*Chemical data for Miami, Cincinnati, and Frederick colloids*

COLLOID	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	LOSS ON IGNI- TION	SiO <sub>2</sub> / R <sub>2</sub> O <sub>3</sub> MOLAR RATIO	BASE EXCHANGE CAPACITY	FREE Fe <sub>2</sub> O <sub>3</sub> REMOVED*	
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>		<i>m.e./100 gm.</i>	<i>gm.</i>	<i>per cent</i>
Miami.....	52.10	21.58	10.51	0.12	9.28	3.12	64.0	2.51	23.8
Cincinnati.....	49.17	24.76	12.10	0.13	10.55	2.57	45.6	4.45	36.8
Frederick.....	46.00	26.43	10.40	0.09	10.46	2.32	35.0	4.93	47.4

\* Removed by biological reduction (1) and expressed as percentage of total Fe<sub>2</sub>O<sub>3</sub> present before reduction, indicated in column 4 of this table.

and also for base-exchange capacity as determined by the titration procedure of Bradfield and Allison (5).

The extracts from the adsorption experiments were analyzed for phosphorus by the colorimetric method of Benedict and Theis (3). The amount of  $\text{H}_3\text{PO}_4$  adsorbed by the colloids was determined by subtracting the amount of phosphate remaining in solution, as determined by analysis, from the total amount originally added.

### RESULTS AND DISCUSSION

The analytical data in table 1 confirm the author's previous suggestion in regard to the relative maturity of the soils from which the colloids were isolated. This relationship is best illustrated by the SiO<sub>2</sub>/R<sub>2</sub>O<sub>3</sub> ratios and the base-exchange capacity values, which are highest for the Miami, representing the youngest stage of maturity, and lowest for the Frederick, the most mature member of this group. Further evidence of this relationship is suggested by the deferration data. By this treatment the Miami, Cincinnati, and Frederick colloids yielded 23.8, 36.8 and 47.4 per cent respectively, of the total Fe<sub>2</sub>O<sub>3</sub> present. It is a well-known fact

that old weathered soils are richer in accumulated products of weathering, especially  $\text{Fe}_2\text{O}_3$ , than are youthful soils, and for this reason they would be expected to yield more soluble iron when reduced.

*Trends in phosphate adsorption by soil colloids*

The data for the several adsorption experiments conducted in this investigation are expressed graphically in the form of curves, in figure 1. In the order

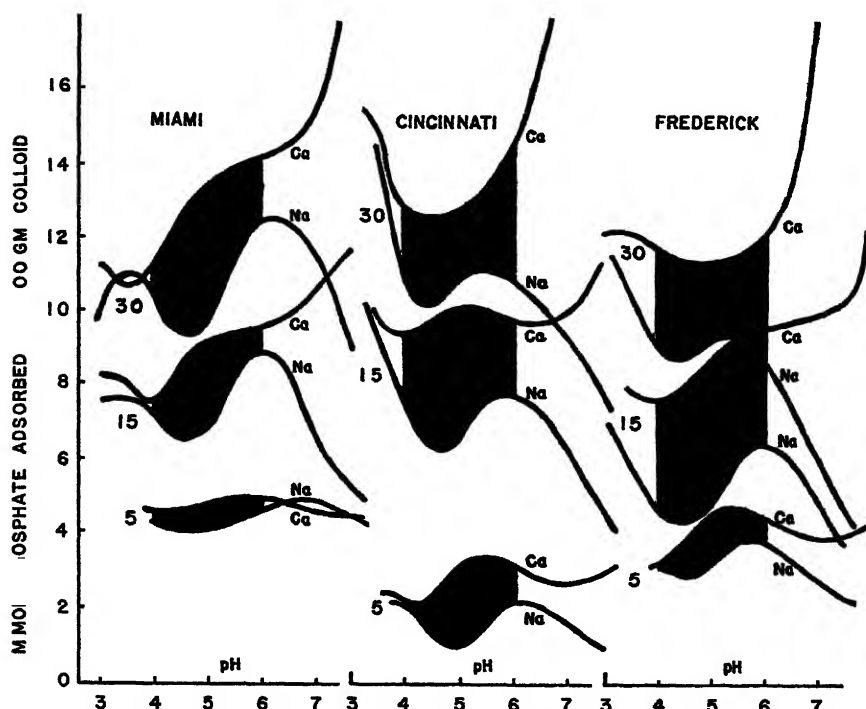


FIG. 1. PHOSPHATE ADSORPTION BY ELECTRODIALYZED MIAMI, CINCINNATI, AND FREDERICK COLLOIDS EACH IN THE PRESENCE OF THREE CONCENTRATIONS OF  $\text{H}_2\text{PO}_4$ , VIZ.: 30, 15, AND 5 MILLIMOLES PER 100 GM. OF COLLOID, WITH ADJUSTMENTS IN pH OVER THE RANGE 3.0 TO 8.0 BY ADDITION OF EITHER  $\text{NaOH}$  ( $\text{Na}$  SERIES) OR  $\text{Ca}(\text{OH})_2$  ( $\text{Ca}$  SERIES)

The shaded area between pH 4.0 and 6.0 for the associated calcium and sodium adsorption curves indicates the effect of exchangeable calcium in retaining phosphate anions.

mentioned they represent the trend of phosphate adsorption by electrodialyzed Miami, Cincinnati, and Frederick colloids, each in the presence of the three concentrations of  $\text{H}_2\text{PO}_4$ , with adjustments in pH over the range 3.0 to 8.0 by additions of either  $\text{NaOH}$  or  $\text{Ca}(\text{OH})_2$ . The phosphate additions made at the rates of 30, 15 and 5 millimoles of the acid per 100 gm. of colloid are hereafter referred to as *high*, *medium*, and *low* phosphate levels, respectively.

*Sodium series.* With  $\text{Na}^+$  as the exchangeable cation the curves of phosphate adsorption present a characteristic maximum and minimum effect. This is

especially true for the Miami colloid, where it is most evident at the medium and high phosphate levels and barely detectable at the low level. The corresponding curves for the Cincinnati and Frederick colloids are somewhat similar to those for the Miami colloid. In general, the first adsorption peak occurs in the pH range of 3.0 to 3.5. Within this pH range and for the high phosphate level the Miami, Cincinnati, and Frederick colloids adsorbed 11.3, 14.6, and 11.7 millimoles of phosphate, respectively. With a decrease in acidity to pH 4.5 a sharp drop in adsorption is noted. The high phosphate retention in the very low pH range of 3.0 to 3.5 strongly indicates adsorption by hydrous Fe and Al oxides (9, 15), especially the former, since its activity in soils has been shown to be much greater than that of Al (7, 8, 14). As suggested by the trend of the adsorption curves, it is significant that whatever agency is active at low pH in these colloidal systems, it becomes less effective in immobilizing phosphate anions as the pH is shifted toward neutrality.

All the curves of phosphate adsorption in the sodium series for the three colloids under study reveal that at approximately pH 4.5 the curves abruptly change direction from a strong downward slope to an equally strong upward slope. It is significant that from the lowest point at pH 4.5 the phosphate adsorption rapidly rises to a second high peak at about pH 6.0. This second adsorption maximum is probably due to aluminosilicate clay minerals present in the colloids which apparently adsorb phosphate by anion exchange similar to that reported by Scarseth (17) for the aluminosilicate in bentonite. Thus the low point of adsorption at pH 4.0 to 5.0, between the two maxima at pH 3.0 and pH 6.0 respectively, appears to be a zone in which the effect of two independent agencies responsible for phosphate adsorption overlap, but neither is very effective. A noticeable decrease in retention of phosphate occurs above pH 6.0 because of the competition afforded by hydroxyl ions for the exchange positions, a competition which becomes more acute with increased alkalinity. The phosphate anions present remain in solution because of the solubility of sodium phosphate.

The data presented in these curves indicate that two independent agencies are responsible for adsorption of phosphate in soil colloidal systems dominated by a monovalent cation such as  $\text{Na}^+$ , but more important than this is the fact that within the reaction range of most arable (podzolic) soils, pH 5.0 to 7.0, the "bentonitic" type of adsorption (17) appears to play an important role in the process. Although soil colloids dominated by Na ions do not simulate soil conditions, studies made with them aid greatly in obtaining a clearer conception of the factors responsible for phosphate adsorption in the absence of divalent cations such as  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  which, as will be shown, influence the adsorption.

It is important to note that at the peak of adsorption at approximately pH 6.0 and in the presence of Na ions the Miami colloid adsorbed 12.6, 9.0, and 5.0 millimoles of the phosphate from solutions containing 30, 15, and 5 millimoles of  $\text{H}_3\text{PO}_4$ , respectively. In other words, where the quantity of phosphate was small its adsorption was complete, a fact which aids in explaining the known high adsorbing powers of the Miami soils for small applications of soluble phosphate fertilizers. In comparison the Cincinnati colloid adsorbed 10.8, 7.7, and 2.2,

and the Frederick colloid, 8.6, 6.3, and 3.7 millimoles of phosphate, respectively. The reason for the low adsorption of 2.2 millimoles for the Cincinnati colloid is not clear. It appears from these data that the aluminosilicate colloid in the youthful Miami soil has a greater adsorption capacity for soluble phosphate than the more mature Cincinnati and Frederick colloids.

*Calcium series.* With  $\text{Ca}^{++}$  as the exchangeable cation in the colloidal systems, a situation which closely resembles soil conditions, the trend of adsorption over much of the reaction range is unlike that in the artificial situation in which  $\text{Na}^+$  was the cation. Comparison of the position and shape of the curves for the Ca series with those for the Na series, for any one of the three colloids, shows that between pH 4.0 and 6.0 a new factor, which was not present in the corresponding Na series, also contributes to phosphate retention. In all cases the curves of the Ca series lie above those of the corresponding Na series, indicating a higher retention of phosphate, the increase in retention apparently due to the influence of calcium. This phenomenon will be considered later in this discussion.

In contrast to sodium phosphate, calcium phosphates are insoluble at high pH values. It has been demonstrated that Ca initiates precipitation of phosphates from solutions slightly above pH 6.0 and that maximum precipitation occurs near pH 7.5 (4). When the amount of phosphate in the colloid suspensions was medium to high the upward slope of the retention curves in the Ca series changes abruptly near neutrality to almost vertical, indicating direct precipitation of the phosphate as the Ca salt. When the phosphate concentration was low the change was less abrupt but otherwise similar. It is to be noted that where the amount of soluble phosphate was low, fixation in the presence of Ca was complete for the Miami colloid within the pH range of 5.0 to 6.0 but that when the phosphate addition was medium or high in amount it was not completely fixed within this reaction range. In contrast, the Cincinnati and Frederick colloids failed to fix all of the phosphate added, even at the low level. Here again, as in the Na series, the Cincinnati colloid exhibited anomalous behavior in adsorbing much less phosphate at pH 6.0 from the low level than the more highly weathered Frederick colloid for reasons that are unknown.

The phosphate adsorption capacity at pH 5.8 to 6.2 of the colloids used in this investigation (Na series) was in the order Miami > Cincinnati > Frederick. Since this is the reverse order of maturity of the soils from which these colloids were obtained, it suggests that weathering slowly deteriorates the phosphate-fixing ability of aluminosilicates, which are mainly responsible for adsorption of phosphate anions within the medium acid to nearly neutral range of pH 5.5 to 6.5.

#### *Influence of exchangeable calcium in phosphate retention*

The influence of exchangeable Ca on the colloid complex in rendering phosphate insoluble has been recognized (13, 16, 17). However, its effect in holding appreciable amounts of phosphorus in a readily accessible form for plant use in acid soils has seemingly not been adequately emphasized in the literature. Mattson and Karlsson (13) regard phosphate so held as "saloid-bound" to distinguish it from phosphate held by anion exchange for silicate or hydroxyl ions.



The Ca ion shares its two valences between the micelle and the monovalent  $\text{H}_2\text{PO}_4^-$  anion.

The phosphate adsorption data herein contained offers not only considerable evidence of the magnitude of phosphate retention by Ca ions, but also some indication of the reaction range over which this phenomenon obtains. For convenience of analysis the curves of phosphate adsorption for the Ca series have been superimposed upon the corresponding curves for the Na series for each of the three colloids. In all cases the Ca curves lie above the corresponding Na curves beginning at approximately pH 4.0 and at all pH values above this point. Since phosphorus is precipitated as the Ca salt in soils, beginning at pH 6.0 (4, 19), attention is directed only to the reaction range of pH 4.0 to 6.0. Insofar as application of these data to agricultural soils is important, the range of 5.0 to 6.0 is probably of greatest concern in phosphate availability.

Considering the divergence between the Ca and Na curves as a measure of the effect of exchangeable Ca in retaining phosphate, it is apparent that this effect is exhibited rather uniformly over the pH range 4.5 to 5.5 at all phosphate concentrations and that it attains a maximum at a pH of approximately 5.0. Using pH 5.0 as a basis for comparison, the retention of phosphate by exchangeable Ca in the presence of low, medium, and high phosphate levels for the Miami colloid are 0.5, 1.7, and 2.8 millimoles per 100 gm. of colloid, respectively. The corresponding values for the Cincinnati are 2.2, 3.1, and 2.0 millimoles, and for the Frederick, 1.5, 4.0, and 2.3 millimoles of phosphate. It is interesting to note that whereas the more highly weathered Cincinnati and Frederick colloids retained somewhat less anion-exchange phosphate by aluminosilicate adsorption than the less highly weathered Miami colloid (adsorption at pH 6.0 for Na series) they exhibit a considerably higher retention of phosphorus by exchangeable Ca.

Ravikovitch (16) has indicated that phosphorus so held is highly unstable and is easily released into the soil solution either by attack of weak acids or as a result of hydrolysis of the Ca from the complex. In view of this fact and of the implication of the data presented, exchangeable Ca is probably an important factor in acid soils in retaining an appreciable amount of phosphate in the most readily available of all of its fixed forms, i.e., in the  $\text{H}_2\text{PO}_4^-$ -Ca-micelle linkage.

#### SUMMARY

A study was made of the phosphate adsorption behavior of inorganic colloids from the B<sub>2</sub> horizon of Miami, Cincinnati, and Frederick silt loams. These soils are podzolic in character and represent stages from youthful to advanced maturity in the order mentioned. The colloids were isolated by sedimentation and were electrodialyzed to remove all mobile ions. Phosphate adsorption experiments were conducted by a slight modification of the technique described by Scarseth (17), a technique especially designed for effective pH control in studies of this nature. The results of this investigation may be summarized as follows:

The curves of phosphate adsorption for the Miami, Cincinnati, and Frederick colloids over the pH range 3.0 to 8.0 exhibit characteristic peaks and depressions. The first peak

of adsorption occurs at pH 3.0 to 3.5 and is believed to be due mainly to the hydrated forms of iron.

A second agency, most active over the pH range 5.5 to 6.5, accounts for a second adsorption peak at approximately pH 6.0. The adsorption at this reaction is undoubtedly due to aluminosilicate clay minerals by anion exchange similar to that obtained by Scarseth for montmorillonite, i.e., a "bentonitic" type of adsorption.

Between the two adsorption maxima at pH 3.0 and 6.0, respectively, a much lower adsorption occurs at pH 4.5, apparently due in part to each of the aforementioned agencies.

Within the reaction range of most arable (podzolic) soils, pH 5.0 to 7.0, the "bentonitic" type of phosphate adsorption (fixation) by anion exchange plays an important role.

Although most of the phosphate in soils is adsorbed by the two agencies mentioned, exchangeable calcium is indicated as an important factor in retaining appreciable amounts of phosphate in acid soils in probably the most available of all of its fixed forms, i.e., in the  $\text{H}_2\text{PO}_4^-$ -Ca-micelle linkage. Evidence of retention in this form over the pH range 4.0 to 6.0, or higher, and of the extent of this type of retention, is presented.

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# CHEMICAL CHARACTERISTICS OF THE GREAT SOIL GROUPS OF CHINA

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Since 1931, soil surveys and laboratory investigations have been conducted by the National Geological Survey of China with the support of the China Foundation for Education and Culture. As an outgrowth of the accumulated works, a comprehensive book was prepared by Thorp (11) in 1936, in which detailed analyses of the soils are given. From 1936 to 1941, more information was obtained on the chemical properties of the soils of China. The present report, which gives the chemical characteristics of the great soil groups, is an abstract from the previous analytical works. A generalized soil map is included. This is reproduced, with some revisions in the western part, from the 1941 revision, by the Soils Division of the National Geological Survey of China (7), of Thorp's map compiled during the years 1933 to 1936.

## MOLECULAR RATIOS OF THE COLLOID FRACTION OF ZONAL SOILS<sup>2</sup>

The desert soils and the very light chestnut soils of inner Mongolia and western Kansu are characterized by high silica-sesquioxide and silica-alumina ratios of 2.7 to 3.3 and 3.3 to 4.5 respectively and by a uniformity of colloid composition throughout the whole profile. Chernozem soils occur chiefly in northern Manchuria and small strips and spots on the border between China proper and inner Mongolia, and on the Tibetan borderlands chiefly in Tsinghai Province and on the norther Szechwan Plateau. The colloids of chernozem have distinctively lower ratios than those of desert soils. The silica-sesquioxide ratio averages 2.42; that of the substratum, 2.60. Shantung brown soils occur on the rolling hills or rough mountains of Shantung, western Hopeh, southern Jiaoning, smaller areas in northwestern Honan and southern Shensi. Their silica-sesquioxide ratio varies from 2.0 to 2.2 and their silica-alumina ratio from 2.5 to 2.9. Gray-brown podzolic soils are widespread, as indicated on the map, in the region just north of Yangtze River, on low hills and mountains. In the parts of Kiangsu extending from Nanking to Soochow and to the Chekiang border, soils of this group are more common than the red earths. The silica-sesquioxide ratio of gray-brown soils ranges from 2.4 to 3.0, and the silica-alumina ratio from 3.1 to 4.0. There has evidently been a downward movement of both iron oxide and alumina, and in consequence the subsoils usually have lower ratios.

Because of the different degrees of laterization, red earths in southern China show a variation in silica-sesquioxide ratio of soil colloid from 0.39 to 1.96. Those appearing on the map as old red earth are more highly laterized than is

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<sup>2</sup> Earlier analytical work on the colloid fraction was published in the book by Thorp (11). Later, a more comprehensive treatment of the subject was given by Hseung (1).



podzolized red earth. T'uerkuan loamy clay of central Yunnan gives lowest ratios, the silica-sesquioxide ratio of its surface layer averaging 0.43 and that of the subsurface 0.76. Yellow earths are more or less podzolized. They occur chiefly on Kweichow Plateau, in western Hunan, in western Kwangsi, and in the mountainous region of eastern Szechwan. Strips of yellow earth have also been found on steep mountains of Jurassic sandstone in Szechwan Basin. The alumina and iron oxide show a similar degree of translocation from horizon A to horizon B. The silica-sesquioxide ratio of the A horizon averages 2.28, whereas that of the B horizon falls to 2.00.

Large areas of purple-brown soils occur in Szechwan Basin and in northern Yunnan. They have silica-sesquioxide ratios of 2.60 to 3.5. Since purple-brown soils are the new weathering products of purple sandstones and shales of Cretaceous and Triassic age, their profiles are usually thin, and the variations of molecular ratios in the profile are indistinct.

South of Chingling and Hwai-ho, rice is planted extensively on all soils of suitable topography. In soils after long-continued rice cultivation, iron is mobilized under anaerobic conditions. Accumulations of iron are usually found in subsoils, often at depths of 20 to 35 cm. The silica-alumina ratio, on the other hand, remains relatively constant in the whole profile.

#### THE pH VALUE AND LIME CONTENT<sup>3</sup>

Gray and brown desert soils usually contain more than 10 per cent calcium carbonate in the surface horizons. Degraded chernozems of central Manchuria have been completely leached of their calcium carbonate. The soils are slightly to moderately acid. Similar noncalcareous soils of neutral to slightly alkaline reaction are found in inner Mongolia, eastern Tsinghai, and northwestern Szechwan. The calcium carbonate content of the surface of dark chestnut soils ranges from 1 to 3 per cent. Shantung brown soils are slightly acid to slightly alkaline, but usually are nearly neutral. A few are sufficiently recalcified to effervesce with dilute acid at the surface. Red and yellow earths of southern China are distinctly acid, and generally have pH values of 4 to 5.8. Some derived from basalt found in central Yunnan are about neutral. Further investigation has

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#### THE SOIL MAP

The less important soil types in a given district can not be located exactly on the map. On the large-scale map, from which this is reproduced, they are designated by placing their legend numbers below that of the major soil type. For example, podzolized red earth of central Hunan is designated by the number 18 (podzolized red earth) over 20 (rice paddy soil). This indicates that scattered areas of rice paddy soil occur in this district. Yellow earth of northern Yunnan is numbered 19 over 22 and 14, showing that small areas of rendzina—22—and gray-brown podzolic soil—14—also occurred.

Areas of Mongolia, Tibet, northern Manchuria, and Sinkiang Province, where information on the soil is limited, have been curtailed.

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<sup>3</sup> Early in 1935, a report by Lee (4) on the pH value and the lime content of the soils of China was published. At that time, investigations in northwestern and western China were limited in extent.

shown that the acid properties of red earths, yellow earths, and gray-brown soils in south China are largely due to the unsaturation of the soil colloid. The acidity of these soils is therefore exchangeable rather than soluble (3). Saline soils of the delta region, Kiangsu, and various scattered places in north China have pH values of about 8 to 9.5. Except for the A horizon of incipient solonetz in Chahar Province, these soils are all strongly calcareous. Most of the calcium carbonate has been leached from the rendzina soils of Kwangsi, but in those from Kweichow and southeastern Szechwan, usually containing 1 to 3 per cent calcium carbonate, the lime can still be detected by applying dilute acid. Both the leached and the unleached rendzinas are about neutral.

Extensive study of gray and brown desert soils collected from western Kansu in 1936–1938<sup>4</sup>, gave more complete information than that heretofore available on the lime content of the soils of this region. Such soils usually contain 10 to more than 25 per cent calcium carbonate. Together with the loessial deposits of Shensi and Shansi, they are the most calcareous soils of China.<sup>5</sup> In this connection, Thorp wrote, "The light chestnut colored soils of northwestern China are derived largely from a very calcareous loess, and the weathering has not been sufficient to leach out the lime." In mountainous regions of the loessial plateau where loess influence is pronounced, chernozems, gray-brown podzolic soils, and other acid soils are found.

The purple-brown soils of Szechwan Basin are, for the most part, calcareous. They may, however, be classified into three groups according to soil reaction; namely, calcareous (pH 7.5 to 8.5), neutral, (pH 6.5 to 7.8), and acid (pH 4 to 6). The distribution of these groups is governed by their parent rocks, which are often interlain strictly in consonance with the geological structure. These soils can be indicated separately on a map only after detailed survey. The lime content of calcareous purple-brown soil is very irregular but is usually over 10 per cent. White crusts often coat the surfaces of structural aggregates. The crusts are composed chiefly of calcium sulfate.

Lime concretions are common in the subsoils and deep substrata in Honan, Shantung, Hopeh, and other places in north China. These, described as "Sa-jong" or "Shachiang,"<sup>6</sup> contain up to 85 per cent calcium carbonate. Concretionary layers have also been found in lower depths of the yellowish clayey soils of Szechwan,<sup>7</sup> which contain up to 60 per cent calcium carbonate.

#### EXCHANGEABLE BASES

Comparatively detailed investigations of exchangeable bases were made on pedalfer or acid soils (2). Gray-brown podzolic soils, red earths, and yellow

<sup>4</sup> A part of the samples sent by Dr. C. Y. Tschau, director of the Geological Survey of Fukien Province, on his return from northwestern China in 1939. [See also Ma (6).]

<sup>5</sup> There are some corrections in the map of lime distribution depicted by Thorp and Lee (11, p. 416).

<sup>6</sup> Indicating lime concentrations of ginger root size. Shachiang soils were first described by Shaw (8) in 1931.

<sup>7</sup> In an earlier report on Chengtu clays, made by Thorp and Dye (9), these soils were described as Chengtu clay of possible loessial origin. Later, Yü (12) expressed a different opinion.

earths owe their acid properties largely to unsaturation. In these soils, the exchangeable hydrogen predominates in the total exchange capacity, ranging from 55 to 80 per cent, and the exchangeable potassium and sodium are approximately equal to calcium and magnesium. The total exchange capacity of these soils is often less than 10 m.e. per 100 gm. Brown earths are nearly saturated, and calcium predominates in the exchangeable bases. Only in the young solonetz soil of Chahar Province are large quantities of exchangeable sodium (about 40 per cent of the total exchange capacity) found. Neutral purple-brown soils are good agricultural soils. They contain 20 to 32 m.e. of total exchangeable bases per 100 gm., whereas acid purple-brown soils often contain less than 5 m.e.

Exchangeable potassium, which is usually regarded as an important plant nutrient, is low in the red earth region of southern China. Exceptions are found, however, in the rice paddy soils occurring in the valleys of Kiangsi and Hunan where the neighboring mountains are of granitic origin. Because of the presence of potassium feldspar, exchangeable potassium is high and many of these soils are productive. Pedocals or calcareous soils in northern China are inferred to be rich in bases, but actual data are few.

#### TITANIUM

Small amounts of titanium are present in all soils. Pedocal soils in northern China usually contain about 0.5 per cent  $\text{TiO}_2$ . Larger quantities, about 1 to 3 per cent, have been found in the red earths of central Kiangsi, Hunan, and Yunnan. Red earths derived from basalt contain an exceedingly high quantity of titanium. A typical profile in the Kunming area, Yunnan, for instance, contains up to 6.15 per cent  $\text{TiO}_2$  in the subsoil.

#### MANGANESE

Like titanium, manganese is present in all soils in minute quantities, often less than 0.1 per cent. Considerable amounts of manganese, however, have been found in the red earths of Kiangsi, Hunan, and Yunnan. On analysis of these samples, the ammoniacal precipitates of sesquioxides appear to have a dark purple tint, and subtraction of the weight of  $\text{Mn}_2\text{O}_3$  from the  $\text{R}_2\text{O}_3$  precipitate becomes necessary.

Very large amounts of manganese are found only in concretions. Analyses of various concretionary materials from red earths of Kiangsi, Hunan, Hupeh, and Kwangsi showed the usual content of  $\text{MnO}$  to be less than 1 per cent. Round black concretions in red earths from limestone of Liuchow, Kiangsi, contain up to 21.62 per cent  $\text{MnO}$ , the highest quantity of manganese ever found in soil materials in this country. Concretions and hardpans from paddy soils also contain high percentages of manganese, usually about 1 per cent. Some, such as the iron hardpan of a paddy soil in Nanchang, Kiangsi, contain as much as 5.58 per cent  $\text{MnO}$ .

#### AVAILABLE PHOSPHORUS AND PHOSPHATE FIXATION

Available phosphorus is estimated colorimetrically from the dilute mineral acid extract.<sup>8</sup> The content of this constituent is closely associated with that

<sup>8</sup> Results obtained by Truog's method.



of lime. Soils of northern China are usually more or less calcareous and give high values of available phosphorus. Many red earths, yellow earths, and other podzolic soils give a negative test or lower values. Actually, we have found no lateritic soils or old yellow earths containing any considerable amount of dilute acid soluble phosphorus. The total phosphorus content of red earths, on the other hand, is not always low. Purple-brown soils, except those belonging to the very acid group, are generally rich in available phosphorus.

All soils, except the very sandy ones, precipitate phosphate from their solutions. The reaction is especially pronounced in highly laterized red earths and in old yellow earths. Six milliequivalents of phosphate in 500 cc. of solution can be completely precipitated by 100 gm. of these soils, and most of the fixed phosphate is retained in soils against the leaching of dilute acid or dilute salt solution (5).

#### FERROUS IRON IN PADDY SOILS

Although the quantitative determination of total ferrous iron in paddy soils seems to be impossible at present, semiquantitative determinations by Morgan's colorimetric method have been carried out extensively in this laboratory. The highest accumulation is usually present in the subsoil, which, on exposure, is readily oxidized. Exchangeable ferric oxide is also associated with ferrous oxide, inasmuch as the former is the expected oxidation product of the latter.

Ferrous iron has been found in all paddy soils during the period of submergence. Its effect on the growth of rice plants, however, remains unknown. In pot culture experiments, daily application of ferrous or ferric sulfate solutions in quantities as high as 20 mgm. Fe per pot gave no variation in growth or yield of rice.

#### SOLUBLE SALTS

Soluble salts are prominent only in saline and alkali soils. Large areas of solonchak soils are found in the Delta region of eastern Kiangsu (10). Examination by the Wheatstone bridge method of a large number of samples collected from this area showed total soluble salt contents generally of less than 1 per cent. Only a few of the samples had values as high as 10 per cent. Detailed analyses show that these salts are chiefly in the form of chlorides and sulfates.

Carbonates and bicarbonates are found only in solonetz soils of Changpei, Chahar, where the soil water gives a red coloration on addition of phenolphthalein. Similar alkali soils are found in scattered areas of northern China, in coastal provinces, and in local spots in southern China, such as those in western Yunnan.

#### ORGANIC MATTER

Large areas of peat soil have been found on the Tibetan borderland<sup>9</sup>, chiefly in northwestern Szechwan and southeastern Tsinghai. They have a sod surface about 10 to 20 cm. deep, in which organic matter<sup>10</sup> is exceedingly high, ranging

<sup>9</sup> A soil survey of this area was made by Yü, who joined the expedition in 1939-1940.

<sup>10</sup> Calculated as  $C \times 1.724$ .

from 50 to over 90 per cent. Organic matter in peat soils is highly humified. About 40 per cent of it is soluble in 4 per cent hot KOH solution.

Chernozem soils found in inner Mongolia and northwestern China have an average organic matter content of about 4 per cent. Humified organic matter in many chernozems extends to more than 40 cm. in depth. Surface soils of rendzinas found in Kiangsi and Kweichow have organic matter contents ranging from 3.5 to 12 per cent. Soils under natural vegetation always have a dark surface high in organic matter. These include gray-brown earths and other mountain soils.

#### SOIL TEXTURE

Soils occurring in loess regions, including light chestnut earths of Shensi and Shansi, are characterized by their silty texture. Results from large numbers of samples collected from this region showed the silt content to be 50 to 75 per cent, which puts them among the most silty soils ever reported in any part of the world. Beyond the influence of loess, soil texture differs in various regions. Gray and brown desert soils in inner Mongolia, northern Kansu, and eastern Singkiang are of coarse texture, containing over 50 per cent sand. In general, soils of southern China have a heavier texture than those of the north, the composition varying with the local soil type.

Claypans of brown and gray-brown podzolic soils in central China contain about 50 per cent clay in their subsurface horizons.

#### SUMMARY

The present report gives a generalized idea of the characteristic chemical properties of the great soil groups of China. A generalized soil map of China is appended.

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# SOIL SOLUTION CONCENTRATIONS AT THE WILTING POINT AND THEIR CORRELATION WITH PLANT GROWTH<sup>1</sup>

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Despite a half-century of research on "soil alkali," a need exists for a semi-quantitative index of the degree of plant injury to be expected from various ranges of soil salinity. It is realized that salinity stresses may be modified or masked by other factors of soil, plant, and climate. Nevertheless, if an approximate quantitative relationship could be established between soil solution concentration and plant growth, it would be of value in the diagnosis of salinity effects.

The purpose of this paper is to show the ranges of soil solution concentration and composition that occur in irrigated soils and their correlation with plant growth. These relationships are compared to those that have been obtained with plants grown in sand and water cultures of controlled salinity. A collection at this laboratory of stock soil samples from important agricultural areas of the West provided an excellent opportunity for making the type of investigation reported here. Plants growing in soils necessarily respond to the actual soil solution concentration and composition and not to the values calculated from an extraction of salts at artificial moisture contents, which may result in extremely erroneous interpretations. This study, therefore, has involved the securing of the soil solutions actually existent at field moisture contents.

It is recognized that the soil solution may not represent the true culture medium of the plant, particularly with respect to nutrients that are slowly released by soils, such as phosphorus and potassium. As regards concentrations of salt, and their effect on plant growth, the soil solution does represent conditions to which plant roots are subjected. The wilting percentage<sup>2</sup> represents the lowest moisture content at which a plant can grow. For a constant amount of salts, the concentration found in the soil solution at the wilting percentage is the maximum to which the plant will be subjected, because of the general inverse relationship between concentration and moisture content. Consequently, all soil solution concentrations discussed here have been referred to the wilting percentage by appropriate calculations. Since most of the soil solutions were obtained at soil moisture contents near the wilting range, changes made in the concentrations by these calculations are relatively small.

<sup>1</sup>Contribution from the U. S. Regional Salinity Laboratory, Bureau of Plant Industry, Agricultural Research Administration, in cooperation with the 11 Western States and the Territory of Hawaii.

<sup>2</sup>Though the term "wilting percentage" is used for brevity, it is understood that wilting takes place over a moisture range, as shown by J. R. Furr and J. O. Reeve in a manuscript entitled, "The range of soil moisture percentages through which plants undergo permanent wilting in some soils from semiarid irrigated areas."

## LITERATURE REVIEW

Harris and co-workers (5) compiled extensive data showing that the osmotic pressure of plant saps was related to the soil environment on which the plants were grown and summarized the earlier literature on this question. They say (5, p. 919): "The salts of the soil may conceivably be detrimental to crop production in two ways: first, chemically, through the toxicity of certain of the constituents; second, physically, through the attainment of an osmotic concentration greater than that which can be tolerated by crop plants."

Recent work on the response of plants to salinity in sand and solution cultures has been summarized by Eaton (4), Hayward and Long (6, 7), and Magistad *et al.* (12). In general, these investigations have shown a linear negative correlation between relative plant growth (based on yields in the base nutrient solution as 100 per cent) and the osmotic pressure of the substrate. Superimposed on this major concentration effect are lesser effects due to the nature of the ions and ionic ratios. Thus Hayward and Long obtained better yield of tomatoes in a nutrient solution concentrated to 3 atmospheres than in the same original nutrient solution with additions of sodium chloride to attain the same osmotic pressure. Furthermore, experiments have shown that differences in temperature and sunlight will modify the growth of plants grown in the same substrate.

Some crops are more tolerant to salt than are others. Kearney and Scofield (8) published an extensive list of crop plants in order of tolerance. The staff of the Salinity Laboratory have shown that garden beets, sugar beets, and cotton, with relative yields of 70 per cent when grown in a substrate of 4 atmospheres, may be classed as tolerant to common salts, whereas wax beans provided less than a 20 per cent yield at this concentration. Yields at 0.5 atmosphere in the base nutrient solution were taken as 100 per cent. As an example of a salt-sensitive plant, and of specific ion effects, Hayward and Long (7), in a recent paper, showed that peaches died at 3.4 atmospheres of chloride salts whereas growth continued at 3.6 atmospheres of sulfate salts.

In a recent experiment with alfalfa, Gauch and Magistad<sup>3</sup> obtained a linear relationship between salt concentration and growth. Yields from the second cutting are reproduced in figure 1.

Linear relationships similar to that shown in figure 1 have been found for most crops tested when plotted in a similar manner. Salt-tolerant crops have a slightly sloping regression line, whereas salt-sensitive crops have a steeply sloping one. Extrapolation of the regression lines for sugar beets and milo, for instance (12), would indicate that growth of these crop plants would cease at about 10 to 12 atmospheres. No sand culture experiments have been conducted at this laboratory at concentrations in excess of 7.7 atmospheres to verify the validity of such extrapolated values. Tottingham (18) in a study of nutrient solutions of varied composition grew wheat at 0.5, 2.46, and 7.63 atmospheres. At the highest value, wheat plants in some cultures were not markedly injured at the

<sup>3</sup>Gauch, H. G., and Magistad, O. C. Growth of strawberry clover varieties and of alfalfa and Ladino clover as affected by salt. [Manuscript.]

end of 24 days. Yield of top plus root at this concentration reached 3 gm. compared with yields of 6 gm. at 2.46 atmospheres. Harris *et al.* (5) showed that *Allenrolfia* and *Salicornia*, two salt-tolerant desert shrubs, grew where the soil water had osmotic pressures of 30 to 38 atmospheres. Two samples of soil water ranging above 45 atmospheres were taken from places devoid of vegetation. Various authors have reported growth of plants and molds in sugar solutions having osmotic pressures above 10 atmospheres. Salt-sensitive plants such as beans die if the substrate concentration exceeds 4 atmospheres.

Very few data have been published in which salt concentrations in solutions from saline soils at low moisture contents are correlated with plant growth. Eaton and Sokoloff (3) report a few analyses of displaced solutions from saline soils. One such soil solution contained a total of 308 m.e. of salts per liter. Orange production on this soil was poor. These authors point out the desirability of using low soil-water ratios to obtain an accurate picture of the composi-

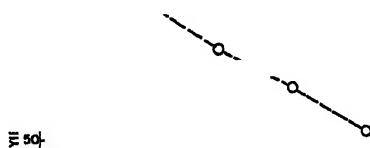


FIG. 1. RELATIVE YIELD OF ALFALFA IN SAND CULTURES OF VARIED OSMOTIC PRESSURES

tion and concentration of the soil solution. Anderson, Keyes, and Cromer (1) have recently made an excellent review of solution concentrations in humid soils. The concentrations of the displaced soil solutions ranged from 600 to 2900 p.p.m.

It has long been realized that the availability of soil water to plants is decreased both by a lowering of the moisture content and by an increase in salinity. More recently, the investigation of energy relations of soil water has made it possible to relate these phenomena on a quantitative basis. Thus, Day (2) has derived a differential equation for the moisture potential of a soil, which is related to the forces involved in a transfer of water from the soil to the plant:

$$d\mu = -sdT + vdP + d\omega$$

in which

$$\begin{aligned} d\mu &= \text{moisture potential term} \\ -sdT &= \text{temperature differential term} \\ vdP &= \text{pressure potential term} \\ d\omega &= \text{osmotic potential term.} \end{aligned}$$

The magnitude of  $-sdT$  is negligible for small temperature differences within the system. Thus, for most conditions, the moisture potential of the soil water is composed of two additive values, the pressure potential and the osmotic potential. The pressure potential relates to the pressure by which water is held in the soil. The osmotic potential is caused by presence of solutes in the soil water. The value of  $vdP$  can be measured by tensiometers, pressure-membrane apparatus, and similar techniques, and  $d\omega$  can be measured by removing the soil solution and determining the activity of the water component, such as by freezing-point depression, or by vapor-pressure lowering.

In sand and solution cultures,  $vdP$  becomes zero, and the moisture potential of the substrate depends on its concentration. In most soils, both terms have appreciable values. Consequently, as in this report, when all soil solution concentrations are calculated to a common tension value (15 atmospheres), the pressure potential term is equal for all soils and the plant response becomes directly related to the osmotic potential.

#### MATERIALS AND METHODS

Seventeen soil samples from the laboratory collection were used in this investigation. Soil solutions were obtained from fifteen of these soils at field moisture by the pressure-membrane method (15).<sup>4</sup> Subsamples of the stock samples, which had been sieved through a  $\frac{1}{8}$ -inch screen, were sprinkled with sufficient distilled water to bring them to predetermined moisture contents. The relative moisture percentages of the fifteen samples varied because some of the samples were used also for other work than that reported here. The moistened samples were kept in air-tight tinned cans in a constant temperature room at 21°C. for at least 2 weeks prior to extraction. At 2-4-day intervals during this period, the samples were removed and mixed by manual working and rolling on a Koroseal mixing cloth. When satisfactory moisture and salt equilibria had been attained, the soils were placed in the pressure-membrane apparatus and the soil solutions were extracted under a nitrogen pressure of 250-270 pounds per square inch (17-18.5 atmospheres).

It has been shown by Richards and Weaver (16) that although the wilting range may vary over a considerable range of soil moisture tension, the moisture held at a tension of 15 atmospheres is usually a reliable index of the wilting point. In this work, the 15-atmosphere value has been used as equivalent to the wilting percentage. This value is determined in the pressure-membrane apparatus by allowing the soil moisture to come to equilibrium with this gas pressure. The fifteen samples were extracted at moisture contents varying from 1.15 to 2.2 times the 15-atmosphere percentage. Usually, coarse soils must be extracted at higher relative moisture contents for satisfactory results and to provide an adequate volume of solution.

The two remaining samples, 207 and 211, were too small to enable extraction

<sup>4</sup>Also Reitemeier, R. F., and Richards, L. A. The reliability of the pressure-membrane method for the extraction of soil solutions, including a comparison with the displacement method. [Incomplete manuscript.]

at field moisture. Solutions were extracted from them at the saturation percentage (17, p. 9) by filtration under suction on a Büchner funnel.

TABLE 1

*Soil solution concentrations in the wilting range and their relationship to plant growth*

SOIL NO.	SOIL TYPE	MOISTURE CONTENT AT			SOIL SOLUTION CONCENTRATION AT 15 ATM. MOISTURE CONTENT				PLANT GROWTH
		Ex-trac-tion	15 atm.	$\frac{1}{2}$ atm.			Osm.P.*	$K \times 10^6$ at 25°C.*	
		%	%	%	m.s./l.	p.p.m.	atm.		
75	Yolo fine sandy loam	15.8	11.7	25.2	32	2,370	1.32	232	Very good wal-nuts, alfalfa
66	Millville loam	13.6	7.6	22.6	41	2,900	1.36	307	Very good wheat
83	Fort Collins loam	14.5	10.1	21.9	44	3,330	1.59	312	Very good wheat, small grains
65	Palouse loam	15.6	10.6	23.7	51	3,950	1.79	344	Very good wheat
77	Silted Superstition sand	14.5	6.6	12.5	57	4,060	1.81†	453†	Good grapefruit
183	Hesperia sandy loam	8.1	4.7	10.6	58	4,260	1.81	525	Good cotton
84	Gila adobe clay	28.9	22.5	41.2	68	4,560	2.02	597	Good cotton
56	Imperial clay	17.4	15.1	29.7	104	6,800	3.1†	840†	Good alfalfa
79	Cajon silty clay loam	24.8	12.0	28.2	132	9,550	4.0†	1,100†	Good wheat
85	Regan clay loam	20.3	11.4	23.2	232	15,600	5.8	1,300	Medium cotton
58	Indio fine sandy loam	12.7	6.2	21.6	235	15,900	7.0†	1,915†	Fair dates
222	Ephrata (?) silt loam	9.6	5.5	27.5	317	21,000	8.6	2,230	Pears and apples retarded
211	Greenhouse soil	121	27.0	49.0	367	25,600	9.1	2,500†	Begonia and ferns dying
86	Fort Collins loam	15.5	12.3	22.4	515	33,200	10.4	2,780	Poor pasture
207	Merced silty clay loam	57.6	15.0	29.0	1,470	88,500	47†	10,700†	Alfalfa failed
57	Imperial clay	27.2	20.4	36.2	2,220	126,000	84††	14,000†	Barren
62	Oasis clay loam	15.2	8.7	25.1	5,700	339,000	235†§	24,200†	Barren

\*Calculated values are corrected for nonlinear variation of osmotic pressure and equivalent conductance with concentration. ( $K$  = specific conductance.)

†Values calculated from measurements made on synthetic solutions.

‡Values include corrections for the change of osmotic pressure with temperature.

§The freezing-point depression exceeded the thermometer scale, and the osmotic pressure was calculated from published freezing-point data for NaCl solutions.

The 15-atmosphere values of all the soils and their moisture contents prior to extraction are shown in table 1.

Determinations made on the soil solutions included ionic constituents, electrical conductivity, and osmotic pressure by means of freezing-point depressions. The chemical analyses were made primarily by the semimicroanalytical methods



described elsewhere,<sup>5</sup> in conjunction with the macromethods used at this laboratory and at the adjacent Rubidoux Laboratory of the Division of Irrigation Agriculture (20). Dissolved salts in terms of parts per million were calculated from the analytical results; because of organic matter, these figures were lower than the total dissolved solids obtained by evaporation. Osmotic pressures were calculated from freezing-point depressions measured with a Beckmann thermometer. For eight soils insufficient samples were available for conductivity and freezing-point measurements. Synthetic solutions were prepared therefore in accordance with the analyses, and these two determinations were

TABLE 2  
*Composition of soil solutions of table 1*  
Results in milliequivalents per liter

SOIL NO.	IONIC CONCENTRATIONS IN EXTRACTED SOLUTIONS									TOTAL SALTS
	Cations				Anions					
	Ca	Mg	Na	K	CO <sub>3</sub>	HCO <sub>3</sub>	SO <sub>4</sub>	Cl	NO <sub>3</sub> *	
75	6.9	11.7	4.6	0.7	0.0	4.7	1.9	2.4	14.3	23.9
66	14.3	7.0	1.4	0.2	0.0	6.7	1.3	3.1	10.2	22.9
83	25.4	3.5	1.1	0.5	0.4	3.7	1.1	1.1	22.5	30.5
65	24.8	8.0	1.2	0.8	0.0	7.6	1.1	2.5	[23]	34.8
77	11.1	4.7	9.8	0.5	1.1	6.5	7.4	5.2	5.7	26.1
183	20.4	6.6	4.3	1.8	0.3	3.4	4.3	5.3	[19]	33.1
84	23.3	6.0	22.7	1.0	0.3	4.1	26.3	14.8	[7]	53.0
56	24.4	19.8	40.9	0.9	0.0	3.1	49.5	27.0	11.3	90.9
79	27.8	14.8	19.2	2.1	0.3	6.7	17.4	10.4	28	63.9
85	45	52	24	9	1	6	53	20	43	130
58	6.4	1.7	100	2.1	5.6	5.6	66.2	28.1	9.0	115
222	25	29	125	2.5	0.2	3.0	128	27	15	182
211	37.4	15.6	25.3	3.9	0.0	2.6	40.7	16.1	[22]	82
86	12.3	210	183	3.3	0.4	12.9	325	31.2	13	409
207	89.9	65.8	224.2	3.5	0.0	2.8	51.0	296	[33]	383
57	787	317	561	2.9	0.0	3.9	19.4	1553	89	1668
62	50	190	2906	97	0.0	4.7	284	2954	18.9	3262

\*Nitrate concentrations in brackets were determined by combining analytical values with appreciable anion deficits, because of apparent loss of nitrate prior to the time of analysis.

made on them. The four methods of expressing concentration comprise those in common use by different investigators.

Concentrations were calculated to the soil moisture content at the 15-atmosphere value by multiplying the actually determined values by the ratio of extraction moisture percentage to the 15-atmosphere percentage. For the osmotic pressure and conductivity calculations, additional factors were used to correct for the nonlinear change of thermodynamic activity and equivalent conductance with concentration. These factors were determined from available

<sup>5</sup> Reitemeier, R. F. 1941 The semimicroanalysis of soil solutions of saline soils. Bureau of Plant Industry, U. S. Department of Agriculture. [Mimeographed.]

thermodynamic data (10, 14) and from conductivity data in the International Critical Tables (13). Osmotic pressures in atmospheres were calculated from freezing-point depressions by the equation derived by Lewis (9), namely,  $O.P. = 12.06\Delta - 0.021\Delta^2$ . For solutions of high concentration, this equation is exactly correct only at the freezing-point, and the calculated values were referred to 25°C. by applying additional corrections involving the heat of dilution (10, pp. 346-363). As these corrections involve various assumptions, some of the reported figures, especially the highest values, are approximations.

#### RESULTS AND DISCUSSION

Tables 1 and 2 contain the numerical results of the investigation. Table 1 includes descriptions of the soil samples, moisture percentages, salt concentrations at the wilting point expressed in four units, and notes on the plant growth. Table 2 comprises the ionic compositions of the extracted soil solutions.

##### *Relationship of soil solution concentration at the wilting point to plant growth*

The data in table 1 show that good or very good plant growth was obtained in the first nine soils. The soil solution of these soils at the wilting percentage had an osmotic pressure of 4 atmospheres or less. The first four soils were from the Experiment Station Farms at Davis, California; Logan, Utah; Fort Collins, Colorado; and Pullman, Washington, respectively. These soils produce very good yields. As an example of salinity concentrations encountered in the soil solution under plant growth conditions, and of their variation with the soil moisture content, specific data on Cajon silty clay loam are given. This soil was extracted at 24.8 per cent moisture, and at this moisture content the soil solution had an osmotic pressure of 2.05 atmospheres. At a tension of  $\frac{1}{3}$  atmosphere, this soil contains 28.2 per cent moisture. Richards and Weaver (16) have shown that the  $\frac{1}{3}$ -atmosphere value is approximately equal to the moisture equivalent. Between irrigations the moisture content of this soil might have varied from about 30 per cent to 12 per cent, and the osmotic pressure of the soil solution from 2 to 4 atmospheres. Very likely the moisture content of this soil was never reduced to the wilting percentage during the growth of the wheat. It seems fair to assume that although 4 atmospheres is given as a limiting value for the osmotic pressure of the soil solution, wheat growth took place mainly in the range from 2 to 3 atmospheres.

Plant growth observations shown in the last column of table 1 were based on local ideas of good crop yields. It is recognized that what may be called a good crop on an area uniformly saline might be considered a mediocre crop in more fertile and less saline lands.

In soils having a soil solution concentration above 4 atmospheres at the wilting point, crop yields were definitely not good even by local standards. At values above 40 atmospheres plant growth failed.

Table 1 also gives values for the conductivity of the soil solutions. On this basis we note that where the conductivity exceeded about 1,200, crop growth diminished; at values between 3,000 and 10,000, growth failed.

Recently Scofield<sup>6</sup> made a survey of soils in the Pecos River Basin of New Mexico and Texas. Soil samples were taken from "locations that appeared to represent the several stages or degrees of soil salinity." These samples were brought to the saturation percentage, the "solution extract" was removed by a filter press, and the extract was analyzed. The saturation percentage is about twice that at field capacity and this in turn is about twice that at the wilting percentage. The water content of these soils at the time of filtering therefore was assumed to be roughly four times the wilting percentage. Scofield concluded that where the solution extracts involve a conductivity of 800, salt-sensitive plants do not thrive, but salt-tolerant crops like alfalfa and cotton do well. Where the conductivity of the solution extracts is above 1,500, these salt-tolerant crops do not do well. The Pecos soils contain much gypsum, and the conductivity of these soil solutions at the wilting percentage probably would be less than expected from conductivities at the saturation percentage corrected for the diminished water content.

It has been customary to correlate plant behavior with the salt content of a soil expressed in terms of percentage or parts per million on a dry soil basis. It is more logical to give salt concentrations on the basis of soil solution rather than of soil. Such values are given in column 7 of table 1. Here we see that where the soil solution concentration at wilting exceeded 10,000 p.p.m., growth was markedly retarded. Where the concentration exceeded 40,000 p.p.m., growth ceased.

It should be noted that in soil 62 the total concentration of salts in the soil solution at the wilting percentage approaches the solubility of sodium chloride in water.

For the benefit of those who wish to make comparisons between plant growth and soil solution concentration in units of milliequivalents per liter, these values are included in column 6 of table 1.

Livingston, in 1942 (11), reviewed the general subject of the effect of salts, salt proportions, and concentration on plant growth. He concluded in general that the concentration of a good nutrient solution affects plants mainly through its osmotic value and that this is modified by the kinds of salt and salt ratios present. He pointed out (11, p. 90), "With continuous flow a good solution may be much weaker than 0.017 *M*, but total concentrations greater than about 0.060 *M* (or about 2.5 atm. osmotic pressure) generally retard water absorption, somewhat as a soil does when too dry for healthy growth."

A fertile soil replenishes plant food to the soil solution and acts like a flowing culture. The concentrations in osmotic values and milliequivalents per liter found in the solutions of soils giving good yields and tabulated in table 1 agree with the conclusions of Livingston.

It should be borne in mind that the soil solution concentrations listed in table 1 are calculated concentrations existing in the soil solution at the wilting per-

<sup>6</sup>Scofield, C. S. 1941 The Pecos River joint investigation 1939-1940. Soil salinity investigation. Bureau of Plant Industry, U. S. Department of Agriculture. [Mimeographed.]

centage, and that the plants were, for the most part, growing at concentrations somewhat below these. The relationships shown in the table between plant growth and salt concentration are of the same order as those obtained by other investigators in sand and solution cultures.

### *Composition of soil solutions*

The composition of the solutions as extracted are shown in table 2. These analyses are included because so few data are available on soil solution composition at low soil moisture contents, and because great variance is shown in the composition of solutions from soils from various parts of the western United States. In general, with increasing total salt content there has been a parallel increase in sodium, sulfate, and chloride concentrations. Of particular interest are the high nitrate values of the first four fertile soils, in which nitrates account for one half or more of the anions present.

About half of these soils contained undissolved gypsum. In the solutions from such soils, the product of calcium and sulfate agreed well with expected values as given by Vanoni and Conrad (19).

In the solutions from soils 75, 85, 222, 86, and 62, the concentration of magnesium exceeded that of calcium. It is usually found that the amount of dissolved calcium exceeds that of magnesium in soil solutions of fertile soils.

### SUMMARY

Seventeen soils representing a wide range of salinity conditions were collected, together with notes on plant growth. Soil solutions of these soils were obtained at moisture contents within normal field range. These solutions were analyzed and the values extrapolated to the 15-atmosphere (wilting percentage) value. Concentrations of salt are given in osmotic units, conductivity units, parts per million, and milliequivalents per liter. The relationship between plant growth and osmotic pressure of soil solution was similar to and of the same order as that obtained in sand culture and solution culture experiments. Above 40 atmospheres concentration, the soils were barren. Normally fertile irrigated soils had a soil solution concentration at wilting percentage of 1.3 to 1.8 atmospheres, conductance values ( $K \times 10^6$ ) of 200 to 350, 2,000 to 4,000 p.p.m. and 30 to 50 m.e. per liter of salts.

The soil solutions as extracted varied greatly in composition. Nitrates formed half the anions in the solutions from fertile soils. In a few solutions the magnesium content exceeded that of calcium.

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# A COMPARISON OF THE RESPONSE OF ALFALFA TO IDENTICAL Ca-K RATIOS IN SOIL AND IN SAND CULTURES<sup>1</sup>

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The response of plants to variations in the ratios of the several nutrient ions in solution culture has been the subject of many investigations. The ultimate aim of all such studies is the improvement of fertilizer practice. But many difficulties arise in applying to the soil the results thus obtained. Numerous attempts have been made, therefore, to develop procedures for the study of plant nutrition under conditions more closely approximating those of the natural soil. The nearest approach to a solution of the problem was that devised by Gedroiz (4) and amplified by Albrecht (1). In its latest modification by Hunter, Toth, and Bear (5), it consists in the production of a H-soil and the replacement of the H in the exchange complex of that soil with basic cations in the proportions desired.

The conditions affecting the plant's uptake of nutrients from the exchange complex of a soil differ in many important respects from those in a culture solution. The concentration of nutrients in the soil decreases gradually with crop growth, whereas with solution cultures a virtually constant supply can be maintained by frequent or continuous renewal. Soil colloids have a powerful buffering effect against reaction changes. Soil nutrients are largely adsorbed by the exchange complex or are present as chemical compounds the solubilities of which are closely related to the H-ion concentration, whereas the nutrients in solution cultures are in the ionic state, freely available to the plant. As a result of fixation, adsorption, and exchange reactions, the soil alters the ratios of the nutrient ions from what they would have been had the salts been merely dissolved in water. In solution cultures the only factor disturbing the nutrient relationships is disproportional absorption by the plant.

The purpose of this investigation was to compare the effects of identical ratios of available Ca and K, when supplied in soil and in solution cultures, on the growth and composition of the alfalfa plant.

## MATERIALS AND METHODS

Six lots of Dutchess loam were so prepared as to have Ca-K ratios of 1:1, 2:1, 4:1, 8:1, 16:1, and 32:1, respectively, in the exchange complex, the other major and minor nutrient elements being supplied in constant amounts. Six-pound portions of each lot of soil, mixed with 15-pound portions of acid-washed sand, were placed in 2-gallon pots without drains. Inoculated Hardistan alfalfa was seeded on March 17, 1941, and the first crop was harvested 83 days later.

<sup>1</sup> Journal Series paper of the New Jersey Agricultural Experiment Station, Rutgers University, department of soil chemistry and microbiology.

More complete details of the preparation of these soils and of the experimental procedures employed with them have been given elsewhere (5).<sup>2</sup>

In the solution culture investigation, use was made of pure quartz sand, as described by Shive and Robbins (6). The sand was placed in 2-gallon drainable pots the diameters of which were approximately the same as those of the pots used in the soil study. Uninoculated alfalfa seed was sown on May 5, 1941, and the first crop was harvested 77 days later. During the first week after seeding, the pots received only distilled water, but thereafter approximately 1 liter of nutrient solution of the desired Ca-K ratio was supplied daily to each culture. The pots were flushed every day with distilled water.

The alfalfa seed used in the two studies were from the same original lot. The ratios of Ca to K investigated in the sand culture<sup>3</sup> were identical with those in the exchange complex of the soil. The plants grown in the sand were supplied

TABLE 1  
*Concentrations of nutrients\* and pH† values of solutions used in sand culture*

Ca-K RATIO	SALT CONCENTRATION					Ca	K	pH
	Ca(NO <sub>3</sub> ) <sub>2</sub>	Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub>	KNO <sub>3</sub>	KH <sub>2</sub> PO <sub>4</sub>	MgSO <sub>4</sub>			
	moles/l.	moles/l.	moles/l.	moles/l.	moles/l.	p.p.m.	p.p.m.	
1:1	0.00282		0.00337	0.00225	0.00225	113	220	5.2
2:1	0.00375		0.0015	0.00225	0.00225	150	147	5.0
4:1	0.0045			0.00225	0.00225	180	87	5.0
8:1	0.0045	0.0005		0.00125	0.00225	200	49	4.1
16:1	0.0045	0.0008		0.00065	0.00225	212	25	3.9
32:1	0.0045	0.00095		0.00035	0.00225	214	14	3.8

\* The trace elements, B (as H<sub>3</sub>BO<sub>3</sub>), Mn (as MnSO<sub>4</sub>), and Fe (as Fe-tartrate), were supplied at rates of 1, 0.5, and 1 p.p.m., respectively. The concentrations of Mg, P, S, and N, in p.p.m., were 55, 70, 72, and 126, respectively.

† The soil pH values for the successive ratios were 6.3, 6.2, 6.1, 6.0, 6.0, and 6.0, respectively.

with N by way of the nutrient solution, whereas those grown in the soil were inoculated with rhizobia and obtained their N principally from the atmosphere. In both soil and sand, four plants were grown in each pot and each treatment was replicated three times. The usual precautions were taken to equalize light and temperature conditions.

The plant tops were harvested at the early bloom stage at a height of about 1 inch above the crown. Dry weights were obtained after drying at 80°C. The harvests from the replicate pots were composited, and they were analyzed by the methods of the A.O.A.C. All Ca-K ratios were calculated on the basis of chemical equivalence.

The composition of each nutrient solution for the six Ca-K ratios is presented both in molar concentrations and in parts per million in table 1. All solutions

<sup>2</sup> The soil-grown alfalfa considered here is that of the first harvest from these soils.

<sup>3</sup> The term "sand culture" refers to the use of a culture solution on sand.

were of uniform total equivalent concentration, each having an osmotic pressure of approximately one-half atmosphere.

# RESULTS AND DISCUSSION

Since the two series of plants were grown in different media and at slightly different—but overlapping—seasons, comparisons must be made on a relative basis. In considering growth data, the values obtained from the six Ca-K ratios in each medium were referred to those obtained from the 1:1 ratio as 100. Similarly, in comparing the chemical composition of the crops, the values obtained from the soil having a Ca-K ratio of 1:1 were taken as 100, all other values being referred thereto.

The absolute and relative values for the heights of the tallest plants at harvest time and for the green- and dry-weight yields of alfalfa from soil and sand culture are presented in table 2. There were great differences in the absolute values of the

TABLE 2

*Heights of tallest plants and green- and dry-weight yields of alfalfa grown in soil and in sand culture\**

Ca-K RATIO	AVERAGE HEIGHT				AVERAGE GREEN WEIGHTS				AVERAGE DRY WEIGHTS			
	Inches		Relative		Grams/pot		Relative		Grams/pot		Relative	
	Soil	Sand	Soil	Sand	Soil	Sand	Soil	Sand	Soil	Sand	Soil	Sand
1:1	31.8	43.6	100	100	62.7	127.7	100	100	14.65	26.25	100	100
2:1	32.6	48.5	102	111	74.3	144.4	119	113	17.54	31.70	120	121
4:1	28.5	43.2	90	99	69.4	142.4	111	111	16.81	31.94	115	122
8:1	31.2	48.0	99	110	70.2	141.1	113	110	16.96	33.63	116	128
16:1	31.6	44.5	100	102	72.9	116.8	117	91	17.29	25.48	118	97
32:1	29.6	41.2	93	94	83.7	74.1	134	58	20.24	17.74	138	68

\* Averages for three replicates in each case.

yields on the two media. For the Ca-K ratios of 1:1, 2:1, 4:1, and 8:1, the green and dry weights of alfalfa produced by the plants in sand culture were approximately twice those produced by the same number of plants grown in soil. For the 16:1 ratio, the sand-culture yield was about 50 per cent greater than that from the soil. For the 32:1 ratio, the yield from the soil was the larger.

A clearer picture of the yields is given when these are compared relatively. The highest dry-weight value, 138, obtained from the soil was produced with the 32:1 ratio. Close similarity was apparent in the values resulting from the use of the 2:1, 4:1, 8:1, and 16:1 ratios. In sand culture, on the other hand, the highest value, 128, was associated with a Ca-K ratio of 8:1, the values decreasing sharply to 97 for the 16:1 and to 68 for the 32:1 ratio. In both media the yield from the 1:1 Ca-K ratio was considerably below the maximum.

One or all of three factors may have been responsible for the low values obtained with the highest Ca-K ratios in sand culture, viz., an insufficient supply



of K, an unfavorable Ca-K ratio, and/or an unfavorable pH of the nutrient solution.

The chemical composition of the two series of plants is presented in table 3. The differences between the K content of the plants grown with Ca-K ratios of 8:1, 16:1, and 32:1 on the two media are small. The nutrient balance sheet (table 5) shows that 67 per cent of the available K was removed in the material harvested from the plants growing in the soil having a Ca-K ratio of 32:1, whereas only 19 per cent of the K was contained in the harvest from the sand culture of the same Ca-K ratio. From this it would appear that a deficiency of K was not responsible for the low yield from the Ca-K ratio of 32:1 in sand culture. The rate at which the solution was supplied, however, was virtually

TABLE 3

*Comparison of chemical composition of alfalfa grown in soil and in sand culture*

Ca-K RATIO	ASH		Ca		K		Mg		R <sub>2</sub> O <sub>3</sub>		P		S		N	
	Soil	Sand	Soil	Sand	Soil	Sand	Soil	Sand	Soil	Sand	Soil	Sand	Soil	Sand	Soil	Sand
<i>Percentage composition</i>																
1:1	9.97	9.92	0.77	0.94	3.30	3.94	0.23	0.32	0.26	0.09	0.37	0.43	0.33	0.27	2.86	3.18
2:1	10.05	9.29	1.11	0.98	2.66	3.24	0.25	0.30	0.35	0.07	0.31	0.41	0.34	0.24	2.87	2.80
4:1	10.13	8.88	1.28	1.18	2.61	2.94	0.29	0.32	0.40	0.08	0.31	0.43	0.36	0.30	2.89	2.95
8:1	9.48	8.14	1.52	1.20	2.16	2.29	0.29	0.30	0.44	0.07	0.30	0.43	0.32	0.28	2.89	2.93
16:1	8.86	7.13	1.62	1.49	1.69	1.81	0.30	0.35	0.40	0.06	0.30	0.46	0.33	0.29	2.92	3.05
32:1	7.39	7.96	1.82	1.71	1.15	1.04	0.34	0.43	0.49	0.05	0.35	0.50	0.30	0.32	2.98	2.95
<i>Relative composition*</i>																
1:1	100	99	100	122	100	119	100	139	100	35	100	114	100	82	100	111
2:1	101	95	144	127	81	98	108	130	134	27	95	110	106	73	100	98
4:1	102	89	161	153	79	89	126	139	154	31	94	115	108	91	101	103
8:1	95	82	198	156	65	69	126	130	169	27	81	122	97	85	101	102
16:1	88	72	210	194	51	55	130	152	154	23	83	133	100	88	102	106
32:1	74	80	236	222	35	32	148	187	188	19	92	142	91	97	104	103

\* Values from 1:1 Ca-K ratio in soil are set at 100.

constant throughout the experiment. During most of the growing period the supply of K was undoubtedly in considerable excess of the requirements, the total amount of that element added during the 77-day period being about five times the quantity contained in the plant tops (table 5). It is possible, however, that during some critical period in the growth of the plants the daily supply of K was insufficient to meet their needs. The nutrient balance sheet (table 5) shows that, of the nutrients available, the plants took from the solution minimum and maximum amounts equivalent to approximately 7 and 26 per cent, respectively, of the K, and 2 and 3 per cent each of the Ca, Mg, and P. They also took 1 and 2 per cent of the S and 6 and 11 per cent of the N. It is obvious that all the nutrients, with the possible exception of K, were supplied in great excess.

The fact that the ratios of Ca to K in the plants grown with a Ca-K ratio of 32:1 were very similar for the two media (3.09 and 3.21 for the soil and the sand

TABLE 4  
*Ca-K ratios in alfalfa plants*

Ca-K RATIO IN SOIL AND IN SAND CULTURE	Ca-K RATIO IN PLANTS GROWN ON SOIL CULTURE	Ca-K RATIO IN PLANTS GROWN IN SAND CULTURE
1:1	0.46	0.47
2:1	0.82	0.59
4:1	0.96	0.78
8:1	1.37	1.02
16:1	1.87	1.61
32:1	3.09	3.21

TABLE 5  
*Nutrient balance sheet\**

Ca-K RATIO	Ca			K			Mg			P		
	AVAIL.†		REM.	AVAIL.		REM.	AVAIL.		REM.	AVAIL.		REM.
	mgm.	mgm.	per cent	mgm.	mgm.	per cent	mgm.	mgm.	per cent	mgm.	mgm.	per cent
<i>Soil</i>												
1:1	3162	112	3.6	6169	483	7.8	439	34	7.7	886	55	6.3
2:1	4102	194	4.8	4004	467	11.7	439	44	10.0	886	55	6.3
4:1	4818	215	4.5	2354	438	18.6	439	49	11.1	886	53	6.0
8:1	5276	257	4.9	1286	366	28.4	439	48	11.0	886	52	5.9
16:1	5539	279	5.1	676	292	43.2	439	51	11.7	886	55	6.3
32:1	5677	367	6.5	346	232	67.1	439	69	15.8	886	70	8.0
<i>Sand culture</i>												
1:1	7910	250	3.1	15380	1030	6.8	3830	80	2.1	4890	110	2.3
2:1	10500	310	3.0	10220	1030	10.0	3830	90	2.4	4890	130	2.7
4:1	12600	380	3.0	6160	940	15.3	3830	100	2.6	4890	130	2.7
8:1	14030	400	2.9	3420	770	22.5	3830	100	2.6	4890	150	3.2
16:1	14860	380	2.6	1780	460	25.9	3830	90	2.4	4890	130	2.7
32:1	15290	320	2.1	960	180	18.8	3830	80	2.1	4890	100	1.9

\* The amounts of available cations in the soil, as shown in this table, represent the quantities replaceable by 0.05 N HCl. One twelfth of the soil in each soil culture was saturated with  $H_2PO_4$ , and the available P represents the difference in total P before and after this was done. The quantities of available nutrients shown for each sand culture were calculated on the basis of an estimated 70 liters of nutrient solution that was supplied to each pot of sand during the 77-day growing period.

† Avail. = Available to plant; Rem. = Removed by plant.

culture, respectively, as shown in table 4), and that the highest yield from the soil was obtained with that ratio (table 2), would seem to indicate that the 32:1 ratio of Ca to K in the sand culture was not in itself very unfavorable.

It is possible that the low yields with high Ca-K ratios in sand culture were due in large measure to an unfavorable pH of the nutrient solution. As shown in table 1, the 16:1 and 32:1 solutions had pH values of 3.9 and 3.8, respectively, whereas for the same ratios in soil the pH value was 6.0. (The low pH values of the solutions supplied to sand cultures in this experiment were due to additions of the acid salt monocalcium phosphate, of which the tenth-molar stock solution had a pH value of 2.8). It has been shown (3) that plants absorb cations with increasing difficulty as the pH values of the culture solution fall below certain levels. Arnon and Johnson (2) report good growth of tomatoes, lettuce, and Bermuda grass in solution cultures throughout the range of pH 4 to 8, but these plants are not so sensitive as alfalfa to acid conditions.

The ash content of sand culture plants was generally less than that of the plants grown on soil. The K and Mg contents of the sand culture plants were slightly higher than those of the soil plants, whereas the Ca content was slightly lower. The  $R_2O_3$  content<sup>4</sup> of the plants grown on soil was three to ten times as great as that of the sand culture plants. The soil, having recently been acid-leached (5), supplied large quantities of available Fe and Al to the plants that were grown on it, whereas the plants of the sand culture received no Al and only small amounts of Fe. An appreciably greater quantity of P was taken up from the sand culture solution than from the soil. This was to be expected, since the P in the sand was freely available in the ionic state, whereas that of soil was adsorbed or fixed, some of it in a relatively insoluble form. The percentage of S was a little higher, and that of N somewhat lower, for the plants on soil than for those on the sand culture. Ca and K were not absorbed by the plants in the ratios in which these elements were supplied, the ratio within the plant being about  $\frac{1}{2}$ :1 and 3:1 for the Ca-K ratios of 1:1 and 32:1, respectively.

It would be possible to devise a comparative test of soil and sand cultures in which all beginning cation ratios would be identical. Accurately to correlate plant responses in soil and sand cultures, this must be done. In the present investigation, however, only the Ca-K ratios were identical, but calculations will show that the trends of the variations of the other cation ratios in the two media were analogous. This report is presented, therefore, for the value it may have in pointing the way toward a method for bridging the gap between the solution-culture approach of the plant physiologist and the more direct but less fundamental approach of the soil investigator in determining the responses of plants to fertilizers.

#### SUMMARY

Alfalfa was grown on soil and in sand culture for 83 and 77 days, respectively, with identical ratios of Ca to K available to the plants. Ca-K ratios of 1:1, 2:1, 4:1, 8:1, 16:1, and 32:1 were investigated.

The yields and chemical composition were compared on a relative basis. There was considerable similarity in the values obtained from the same ratios

<sup>4</sup> By  $R_2O_3$  is meant the combined weights of Fe and Al phosphates and oxides in the plant

in the two media, particularly for the ratios 1:1, 2:1, 4:1, and 8:1. The highest yield from the soil was obtained with the highest Ca-K ratio, 32:1. The highest yields, both absolute and relative, from the sand culture were obtained from the first four ratios, the yields decreasing sharply at Ca-K ratios of 16:1 and 32:1. The low yields for the highest ratios in sand culture were attributed largely to an excessively low pH of the nutrient solution.

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PLATE 1

COMPARISON OF ALFALFA RESPONSE IN SOIL AND SAND CULTURE

Fig. 1. Soil culture.

Fig. 2. Sand culture.

Pot numbers were identical in the two investigations. Photographs were taken on harvest dates.

Ca-K Ratio	Pot
1:1	1
2:1	4
4:1	7
8:1	10
16:1	13
32:1	16



FIG 1

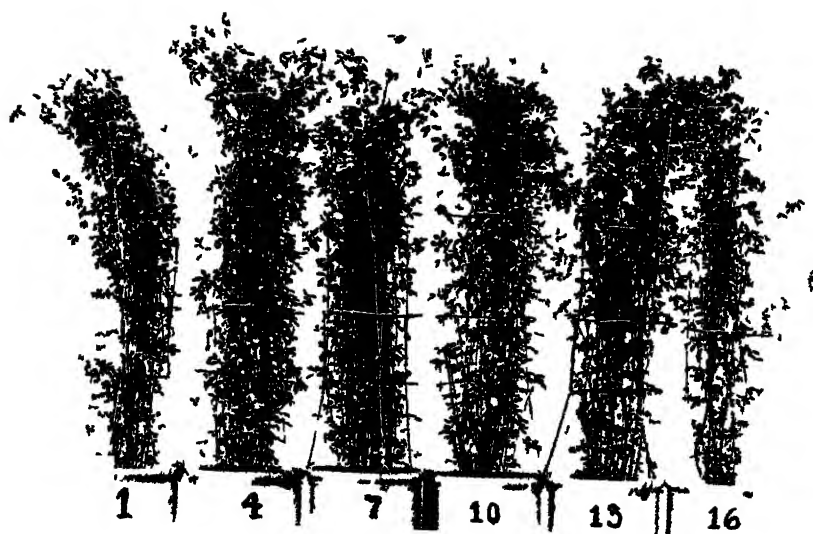


FIG 2



# THE SUITABILITY OF WATER PURIFIED BY SYNTHETIC ION-EXCHANGE RESINS FOR THE GROWING OF PLANTS IN CONTROLLED NUTRIENT CULTURES<sup>1</sup>

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The need for large quantities of low-cost distilled water free from heavy-metal contamination, for use in plant nutritional studies, led to an investigation of the quality of water purified by means of synthetic-resin ion exchangers. These resins are being manufactured on a commercial scale,<sup>3</sup> and suitable equipment for producing water of distilled quality is available.<sup>4</sup>

The principle of the ion-exchange process is as follows: The water to be purified is first passed through a hydrogen-form cation-exchange resin, where the cations are exchanged for hydrogen ions. The water now containing free acids is passed through an anion-exchange resin, which absorbs the anions and releases hydroxyl ions. Bicarbonates and carbonates are converted to carbonic acid, which can subsequently be removed by aeration.

## LABORATORY PREPARATION OF ION-EXCHANGE WATER

A small laboratory unit similar to that described in literature<sup>5</sup> of The Resinous Products & Chemical Company, was set up. This unit consisted of two vertical Pyrex-glass tubes, 3.5 by 120 cm. The bottom of each tube was fitted with a one-hole rubber stopper. In this was inserted a glass filter tube in which was sealed a coarse-fritted-glass disk. Two inches of acid-treated, washed Ottawa sand was added, and each tube was half filled with the appropriate ion-exchange resin.

The synthetic ion-exchange resins used were Amberlite IR-100, cation exchanger, and Amberlite IR-4, anion exchanger. These resins were pretreated with 4 per cent HCl and 2 per cent Na<sub>2</sub>CO<sub>3</sub> solutions, respectively, and were then washed with distilled water until free from electrolyte, as directed by the manufacturer. The bottom of the cation-exchange tube was connected to the top of the anion-exchange tube by the necessary glass- and rubber-tube connections.

<sup>1</sup> Paper No. 479, University of California Citrus Experiment Station, Riverside, California.

<sup>2</sup> Associate, assistant chemist, and associate professor of agricultural chemistry and associate chemist in the experiment station, respectively.

<sup>3</sup> The Resinous Products & Chemical Company, Philadelphia, Pa., manufactures these resins. We are indebted to Edward R. Mueller, of this company, for literature describing the uses and properties of the resins, and for the samples with which we have experimented.

<sup>4</sup> Water-purification equipment utilizing these resins is manufactured by The Illinois Water Treatment Company, Rockford, Illinois. By the proper choice of equipment, heavy-metal contamination can be avoided. Units capable of producing 150 to 5,000 gallons an hour are available, and the cost of purification is much less than that involved in distillation.

<sup>5</sup> The Resinous Products & Chemical Company 1941 The Amberlites. The Resinous Products & Chemical Company, Philadelphia, Pa.



## REMOVAL OF TRACE-ELEMENT CONTAMINANTS FROM DISTILLED WATER

The first experiment was carried out to determine whether the trace-element contaminants in laboratory-distilled water could be reduced by passage through the cation-exchange resin. Distilled water from a laboratory tap was passed through the hydrogen-saturated cation-exchange resin at a rate of 8 liters an hour and collected in Pyrex bottles. A sample of this first-passage water was saved for analysis; the remainder was passed through the cation-exchange resin four more times. Another sample of distilled water was redistilled in an all-Pyrex-glass still. Sufficient samples of these various waters were evaporated to small volumes in silica dishes, transferred to Pyrex Erlenmeyer flasks, and acidified with  $\text{H}_2\text{SO}_4$ . A small quantity of  $\text{CdSO}_4$  was added, and precipitation by  $\text{H}_2\text{S}$  was carried out. The precipitate was removed, and its composition was determined spectrographically. The results are shown in table 1.

It is evident that the principal heavy-metal contaminants (Cu, Pb, and Zn) in the laboratory-distilled water were effectively removed by passage through

TABLE 1

*Removal of heavy-metal contaminants from distilled water by redistillation and by passage through cation-exchange resin*

SAMPLE	CONSTITUENTS		
	Cu	Pb	Zn
	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>
Laboratory-distilled water.....	0.2000	0.0550	0.02
Redistilled water*.....	0.0016	0.0025	0.00
Ion-exchange water, after one passage.....	0.0035	0.0015	0.00
Ion-exchange water, after five passages.....	0.0000	0.0010	0.00

\* Laboratory-distilled water redistilled in all-Pyrex-glass still.

the cation-exchange resin. Water of greater purity, with respect to these metals, was produced by repeated passage through the resin than was obtained by redistillation in the all-Pyrex-glass still. For culture work with micronutrients, for which high-purity water is necessary, it appears that this method offers interesting possibilities.

## PURIFICATION OF TAP WATER BY PASSAGE THROUGH SYNTHETIC ION-EXCHANGE RESINS

In this experiment, ordinary tap water was passed through the ion-exchange equipment described, at a rate of 4 liters an hour. The conductivity of the exchange water was comparable to that of the laboratory-distilled water. Liter samples of the exchange water and of the distilled water were evaporated in platinum dishes, and determinations of total solids, loss on ignition, silica, and nonvolatile residue were made; other portions were analyzed for major constituents such as calcium and magnesium. Still further samples of tap water and of exchange water were evaporated in silica dishes, and the residues were

spectrographed to determine the contents of trace elements. The results of these analyses are shown in table 2.

TABLE 2

*Composition of tap water before and after passing through cation- and anion-exchange resins, in comparison with distilled water*

	TAP WATER	DISTILLED WATER	ION-EXCHANGE WATER
	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>
Total solids at 356°F.....	309.0	2.0	27.0
Loss in total solids upon ignition (1000°F.).....	....	0.6	3.30
Silica.....	24.0	0.0	22.80
Nonvolatile residue.....	....	1.6	0.90
Bicarbonate.....	171.0	....*	ND†
Calcium.....	48.0	....	0.01
Carbonate.....	0.0	....	ND
Chloride.....	21.0	....	ND
Magnesium.....	6.0	....	0.50
Nitrate.....	8.0	....	....
Potassium.....	3.0	....	ND
Sodium.....	24.0	....	ND
Sulfate.....	28.0	....	....

*Spectrographic examination of residue containing silica‡*

Aluminum.....	0.01	....	0.0003
Barium.....	0.015	....	0.002
Boron.....	0.1	....	0.08
Chromium.....	0.004	....	0.002
Copper.....	0.008	....	0.002
Iron.....	0.05	....	0.002
Lead.....	0.002	....	0.001
Lithium.....	0.010	....	ND
Manganese.....	0.001	....	0.002
Molybdenum.....	0.01	....	ND
Nickel.....	ND	....	0.002
Silver.....	0.0005	....	0.0002
Strontium.....	0.120	....	0.001
Tin.....	ND	....	0.002
Vanadium.....	0.100	....	ND
Zinc.....	ND	....	0.02

\* Leaders indicate data not determined.

† ND = none detected.

‡ These results are approximations; some may be as much as 50 to 100 per cent in error.

Aside from its silica content, the exchange water is comparable in quality to distilled water. The nonvolatile residue, after removal of silica, was 1.60 p.p.m. in the distilled water, and 0.90 p.p.m. in the exchange water. The exchange resins do not take out silica, and no claim for this is made by the manufacturer. For some chemical laboratory purposes, the silica would, of course, be objection-

able, but various patented methods<sup>6</sup> have been devised for its removal and might possibly be used in connection with the exchange-resin equipment.

The exchange water (table 2) contained 3.30 p.p.m. of volatile substances, probably organic material dissolved from the resins. The nonvolatile portion of the exchange water, after removal of silica, proved to be largely magnesium. Of the trace elements contained in the tap water, iron, aluminum, molybdenum, copper, strontium, barium, vanadium, and lithium were significantly reduced by passage through the resins. Further removal of these could no doubt have been achieved by repeated passage of the water through the cation-exchange resin.

#### EFFECT OF ION-EXCHANGE WATER ON CITRUS PLANTS GROWN IN CONTROLLED NUTRIENT CULTURES

As a final test of the suitability of ion-exchange water for plant-culture work, two cultures using 8-liter cylindrical Pyrex-glass jars were set up in the greenhouse. Each culture contained one lemon cutting and two Valencia orange cuttings.

A large volume of a fairly concentrated base-nutrient solution containing calcium, magnesium, potassium, sodium, chloride, nitrate, sulfate, and phosphate was purified in a 140-liter tile container by the addition of enough  $\text{Ca}(\text{OH})_2$  to bring about a phosphate precipitation. After the precipitate had settled, 5 liters of this solution was siphoned into each of the two Pyrex jars, and the reaction was adjusted to pH 4.5 with redistilled  $\text{HNO}_3$ . The volume of one container was made to 7.5 liters with the exchange water; that of the other container was made to the same amount with redistilled water from an all-Pyrex-glass still. A small amount of phosphate was added, and the composition of the final solution thus prepared, in milliequivalents per liter, was: Ca, 6.88; Mg, 3.77; K, 2.79; Na, 0.1; Cl, 0.1;  $\text{NO}_3$ , 10.01;  $\text{SO}_4$ , 2.5; and  $\text{PO}_4$ , 0.33. Mn, Zn, and B were added to give 0.1 p.p.m. each, and purified  $\text{FeSO}_4$  was added thrice weekly. The pH value was maintained between pH 4.0 and 5.0 by the addition of redistilled  $\text{HNO}_3$ . New solutions were prepared every 28 days.

The water lost by transpiration and evaporation was compensated for by additions of exchange water to the one culture and of redistilled water to the other. The plants were grown for 8 months. The amount of water used by these plants after they had become established was fairly large, the quantities added during the 28-day periods between renewals being five to six times the original volume of the cultures. Hence, any toxic organic or inorganic constituent coming from the exchange water would be expected to accumulate, either in the solution or in the plant, and, in the course of 8 months, to cause injury. At no time during the experiment, however, was there any sign of toxicity in either the orange or the lemon cuttings growing in the exchange-water culture. If anything, the plants supplied with this water made slightly more top and root

<sup>6</sup> Liebknecht, O., and Gerb, L. (to The Permutit Co.) 1942 Removing silica from water. (U. S. Patent No. 2,267, 831.) Abs. in *Chem. Abs.* 36: 2658.

The Permutit Co. 1942 Removing silica from water. (British Patent No. 539,884.) Abs. in *Chem. Abs.* 36: 4246.

## ION-EXCHANGE WATER FOR PLANTS

growth than did those supplied with the redistilled water, but the difference, if significant at all, was slight. The tops and roots of both sets of plants are shown in figure 1. An indication of health in citrus roots is the production of long white laterals and a light color of the older roots. As may be seen from the illustration, both sets of roots were of this character.

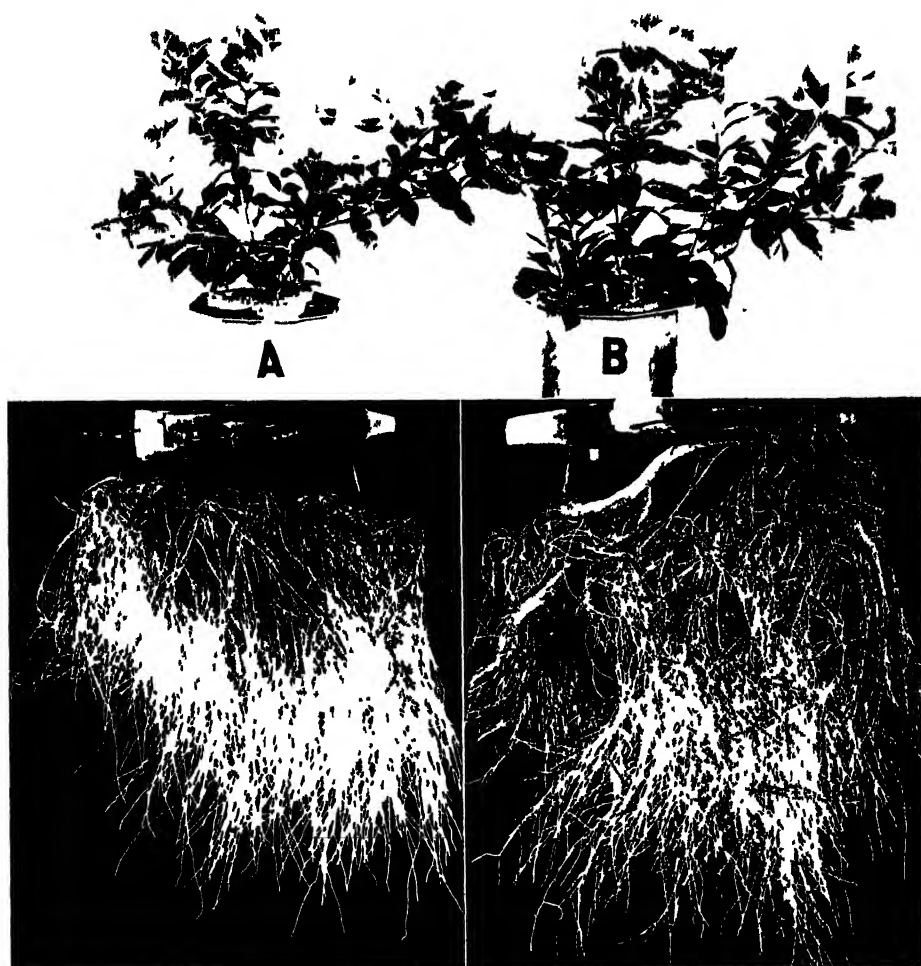


FIG. 1. TOPS AND ROOTS OF CITRUS CUTTINGS GROWN IN SOLUTION CULTURES: A, SUPPLIED WITH WATER REDISTILLED IN AN ALL-PYREX GLASS STILL; B, SUPPLIED WITH ION-EXCHANGE WATER

### SUMMARY AND CONCLUSIONS

The results of experiments to determine the suitability, for plant growth, of water purified by passage through synthetic ion-exchange resins, show that water of high quality can be obtained. Objectionable traces of copper and other heavy metals can be removed from distilled water by passage through a hydrogen-sat-

urated cation-exchange resin. The purity of the water is increased by repeated passages through this resin.

Water comparable in quality to distilled water, except for silica content, can be prepared from ordinary tap water by passage through both cation- and anion-exchange resins. This water was found to be suitable for use in plant nutritional studies.

The cost of purifying our local tap water with equipment having a capacity of 300 gallons an hour, not considering the original investment, is estimated at somewhat less than 0.1 cent a gallon.

# THE ACTIVITY OF SUBSURFACE SOIL POPULATIONS<sup>1</sup>

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Soil organisms in general exhibit considerable versatility in performance and viability through periods of physical adversity, such as desiccation, waterlogging, or freezing. In the words of Cutler and Crump (1), "... a population has been developed by evolution which is on the whole so unspecialized that almost any substance that finds its way into the soil either naturally or as a result of agricultural practice will eventually be incorporated in the general soil economy." Almost all researches on soil populations have been carried out on the organisms from surface or A horizon samples. Since the normal diet of the subsurface soil population is composed of soluble or dispersible products carried down from the A horizon or of root-derived material, or of both, the versatility of the populations in the B and C horizons may not be so great. Yet by erosion the subsurface horizons are exposed, in which case they then receive a different type of energy material, namely, agricultural residues. For this reason it is pertinent to know the adaptability of microorganisms in the B and C horizons in the decomposition of plant residues.

Information as to the potentialities of the subsurface populations is not given by the analytical type of bacteriological investigation in which isolation and classification are the main objectives, nor is much direct help provided by quantitative studies in the form of plate counts.

As reported in a previous publication (3) on the activity of the microflora in various horizons of several soil types, the amount of CO<sub>2</sub> evolved from incubated soil samples was found to decrease with depth and the maximum rate of CO<sub>2</sub> evolution to occur during the first day in almost all instances. On addition of 1 per cent cornstalks to these soils the peak rate of CO<sub>2</sub> evolution was attained more and more slowly with increasing depth and also the rate at the maximum decreased, in general, with depth. This was believed to be due not only to a progressive reduction in the size of the population, but also to a decrease in adaptability to the organic matter added. The differences were large. For example, the total amount of CO<sub>2</sub> evolved from 100 gm. soil plus cornstalks during 14 days' incubation ranged from 1048 mgm. for an A horizon Fayette sample to 252 mgm. for a B<sub>3</sub> horizon Marion sample. It was suggested that the difference in the potentialities of the populations in the several horizons was due to the existence of an interrelationship between the stable microflora and the amount and the availability of the soil organic matter present.

The purpose of the study reported here was to investigate further the reasons for the observed differences in microbial activity within the profile and for the apparent decline in versatility and adaptability with depth.

<sup>1</sup> Journal paper J-1080 of the Iowa Agricultural Experiment Station, Ames, Iowa. Project 590.

<sup>2</sup> Formerly research fellow, and research professor of soils, respectively.

## EXPERIMENTAL

Most of the profiles used in these studies have been described (3). The soil number in the Iowa collection and the horizon and depth of soil samples used are as follows:

SOIL	NUMBER	HORIZON	inches
Marshall silt loam	P54 - 1	A	0- 2
	- 6	A	16-20
	- 9	C	30-36
	- 10	C	36-43
	- 12	C	50-58
Fayette silt loam	P109- 3	A <sub>1</sub>	0- 1½
	- 9	B <sub>2</sub>	18-24
Marion silt loam	P8 - 1	A <sub>1</sub>	0- 6
Clarion silt loam	P55 - 1	A <sub>1</sub>	0- 3
Clinton silt loam	359	A <sub>1</sub>	0- 3
Clinton silt loam	362	A	0- 3
Shelby loam	363	A	0- 3
Lindley loam	364	A	0- 3

*Evolution of CO<sub>2</sub> from soils plus complete or water-extracted cornstalks*

On the addition of cornstalks to soil, the rate of CO<sub>2</sub> evolution reaches a maximum usually within the first 24 to 48 hours and thereafter declines sharply. Information as to that fraction of the cornstalks contributing largely to this peak was obtained by comparing the CO<sub>2</sub> evolution from the original cornstalks and from hot-water-extracted cornstalks in three different surface soils (fig. 1). The analyses of the cornstalks employed are given in table 1. In each case, 1 gm. of the sterile organic material in 100 gm. of soil was used. To ensure a sufficiency of nitrogen, enough ammonium sulfate was added to bring the total nitrogen level up to 1.75 per cent of the complete or the extracted cornstalks present.

TABLE 1

*Chemical analyses of cornstalks used in carbon dioxide evolution experiments*

CONSTITUENT	PER CENT*	CONSTITUENT	PER CENT*
Total nitrogen.....	1.26	Xylan in cellulose.....	13.86
Total carbon.....	43.40	Soluble in hot water.....	20.18
Cellulose.....	45.16	Soluble in hot 3 per cent H <sub>2</sub> SO <sub>4</sub> .....	42.34
Lignin.....	16.16	Furfuraldehyde yield	
Furfuraldehyde yield		From residue of hot-water extrac-	
From original cornstalks.....	16.51	tion.....	14.97
From cellulose.....	8.94	From residue of hot 3 per cent H <sub>2</sub> SO <sub>4</sub>	
		extraction.....	8.13

\* Of oven-dry material.

The peak  $\text{CO}_2$  evolution occurred during the first day from soil plus cornstalks and on the third day from soil plus extracted cornstalks. Not only was the time lengthened to attainment of the peak rate but also the magnitude of the rate at the peak was much reduced by hot-water extraction. This must mean that the initial high peak rate of  $\text{CO}_2$  evolution from soil plus cornstalks is largely at the expense of the water-soluble constituents, which comprise about 20 per cent of the total cornstalks (table 1). The delayed peak previously reported in the Marion and Fayette subsurface samples is thus the more remarkable since it indicates that up to 3 days was required to build up a population capable of

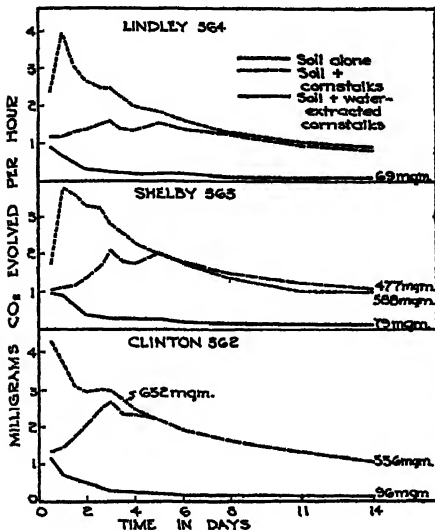


FIG. 1

FIG. 1. EFFECT OF WATER EXTRACTION OF CORNSTALKS ON HOURLY RATES AND CUMULATIVE TOTALS OF CARBON DIOXIDE EVOLVED FROM SUCH PLANT MATERIAL INCORPORATED IN THREE SURFACE SOILS

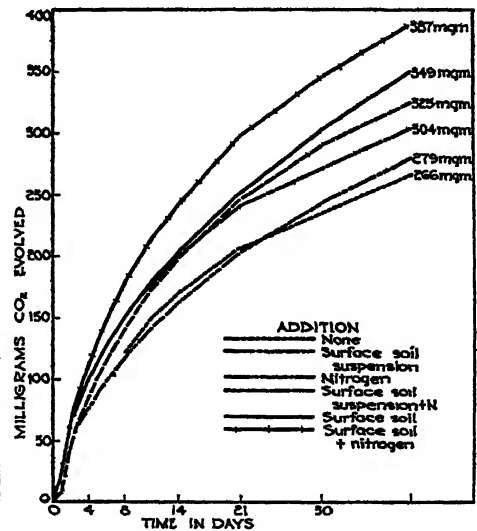


FIG. 2

FIG. 2. EFFECT OF ADDITION OF MARSHALL SURFACE SOIL OR SURFACE SOIL SUSPENSION ON CUMULATIVE TOTALS OF CARBON DIOXIDE EVOLVED FROM CORNSTALKS INCORPORATED IN MARSHALL SUBSURFACE SOIL (36-43 INCHES)

rapidly decomposing even the presumably highly available water-soluble constituents. The significance of this will be discussed later.

*Evolution of  $\text{CO}_2$  from subsurface soils plus cornstalks to which surface soil or sterile and nonsterile surface soil suspensions had been added*

The inability of the subsurface samples rapidly to begin the decomposition of added cornstalks led to the belief that the populations of such samples were quantitatively smaller than those of the surface samples. Further, since the rate of  $\text{CO}_2$  evolution dropped rapidly after the peak was attained and the total evolution was much lower, the subsurface populations must also differ greatly qualitatively. If these assumptions are correct, the addition of a small amount of surface soil or surface soil suspension to subsurface soils plus cornstalks, by



introducing a more vigorous flora, should cause a large increase in  $\text{CO}_2$  production on incubation of the samples.

The results of an experiment testing the inoculation of subsurface soil with surface soil are given in figure 2. If surface soil was used, 2.5 gm. was ground to pass a 20-mesh sieve and mixed thoroughly with 47.5 gm. of the subsurface soil. If surface soil suspension was used, surface soil ground to pass a 20-mesh sieve was shaken with water, and an aliquot representing 2.5 gm. of soil was added to 50 gm. of subsurface soil. Before addition of any moisture, 0.5 gm. of cornstalks was thoroughly mixed with the soil. Since nitrogen might be a limiting factor in the decomposition of cornstalks in subsurface samples, 1 per cent nitrogen as  $(\text{NH}_4)_2\text{HPO}_4$  on the basis of the cornstalks was added in solution to a duplicate set of samples. The cornstalks initially contained 1.26 per cent nitrogen (table 1) which is believed to be adequate for normal aerobic decomposition in the absence of soil. The moisture content was brought up to optimum in all instances.

The first point of note from these curves is the increase in  $\text{CO}_2$  evolution caused by the addition of inorganic nitrogen, particularly after the fifth day of incubation. In all subsequent experiments of this series additional nitrogen was added to bring the nitrogen level up to 2.26 per cent on the basis of the cornstalks.

The inoculation of the subsurface sample of Marshall silt loam (P54-10) with the surface sample (P54-1) stimulated  $\text{CO}_2$  production slightly though not to the extent that might have been expected had the introduced topsoil population behaved as it did alone. The total  $\text{CO}_2$  production was still much below that evolved from P54-1 with cornstalks, if the amount originating from the soil organic matter is taken into consideration. Almost half the increase in the  $\text{CO}_2$  evolution by this treatment in 14 days' incubation can be accounted for by the  $\text{CO}_2$  evolved from the soil organic matter in 2.5 gm. of P54-1.

To test further the possibility of inoculating subsurface soil with surface populations, Marshall silt loam (P54-10) was inoculated with soil, soil suspension, and sterile soil suspension from several different surface soils according to the procedure described for the last experiment. Sterile surface soil suspensions were included to control any possible effect of nutrients introduced with the soil suspension as distinct from the effect of the populations. Although excellent agreement was always obtained between duplicates in the experiments previously reported, the duplicates in the inoculation experiments were not always so good. Typical results obtained with two soils are given in table 2 as cumulative totals at various intervals. If the average  $\text{CO}_2$  production had been plotted as time-rate curves, erroneous conclusions might have been reached. The addition of surface soil caused increases in  $\text{CO}_2$  evolution in both cases, but the magnitude of these was far less than might have been expected. In neither case did the additions of suspensions of surface soils cause a clear-cut increase in  $\text{CO}_2$  production. The additions of sterile suspensions, on the other hand, caused a definite depression in the  $\text{CO}_2$  production for the first few days of the incubation. This effect, however, did not continue, and after 40 days the totals were

not significantly different from the control subsurface sample. The time elapsing until the occurrence of peak CO<sub>2</sub> evolution was reduced by the additions of surface soils, but was not consistently affected by addition of either the sterile or the nonsterile surface soil suspensions.

From the last two experiments, it was apparent that the introduced populations from surface soil did not cause a rapid decomposition of cornstalks in a subsurface soil environment. There was still the possibility that this was due to the introduction of too small a number of organisms. To determine whether this was the case, 5 gm. of each of several surface soils was added to 95 gm.

TABLE 2

*Evolution of carbon dioxide from Marshall subsurface sample plus cornstalks with addition of surface soil or sterile and nonsterile surface soil suspensions*

FORM OF SOIL INOCULUM	CO <sub>2</sub> EVOLVED* DURING INCUBATION					TIME OF PEAK	RATE AT PEAK
	1 day	3 days	8 days	14 days	40 days		
	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>mgm.</i>	<i>hrs.</i>	<i>mgm./hr</i>
None	11	70	124	184	310	36	1.9
	10	65	122	181	294		
<i>Marion silt loam (P8-1)</i>							
Soil	19	78	150	202	325		
	13	67	144	197	317		
Soil suspension	8	59	134	197	311	30	1.5
	13	64	139	200	322		
Sterile soil suspen- sion	5	55	120	183	307	36	1.4
	4	57	121	184	302		
<i>Clarion silt loam (P55-1)</i>							
Soil	33	97	172	219	338		
	24	99	176	225	348		
Soil suspension	13	66	128	183	299	24	2.0
	9	56	129	195	301		
Sterile soil suspen- sion	3	50	114	180	297	30	1.5
	6	51	116	172	280		
36							
1.7							

\* On basis of 0.5 gm. cornstalks, 50 gm. air-dry P54-10 and suspension from 2.5 gm. surface soil, or 47.5 gm. P54-10 and 2.5 gm. surface soil.

of sterile quartz sand plus 1 gm. of cornstalks, and surface soil suspensions equivalent to 5 gm. of the respective surface soils were added to 100 gm. of sand plus 1 gm. of cornstalks. The moisture was made uniform at the optimum level. Determinations of CO<sub>2</sub> production were made frequently, but only the total CO<sub>2</sub> evolution at 14 days, the time of the peak, and the rate at the peak are shown in table 3.

Inoculation by addition of either soil or soil suspension provided a population large enough to decompose the cornstalks rapidly. There was no evidence that inoculation by direct addition of soil was superior to the inoculation by means

of a suspension. In fact, there was some evidence that the suspension population was superior at the beginning, since the peak rate in every case was higher than that for the corresponding soil inoculation.

Since the soil or soil suspension inoculant carried a sufficient population for rapid and extensive decomposition, there must have been some factor in the subsurface sample (P54-10) preventing rapid development and decomposition.

To test further the possibilities of subsurface soil inoculation with surface soil populations, other experiments were carried out with the Fayette 18-24-inch sample (P109-9). The total CO<sub>2</sub> evolution at several intervals, the rate of CO<sub>2</sub> production at the peak, and the time of peak CO<sub>2</sub> production from this sample plus cornstalks inoculated with three different surface soils, soil suspensions, and sterile soil suspensions are given in table 4. The inoculation with surface soil caused increased CO<sub>2</sub> production over the control, though the increase was by no means the amount that might have been expected from the data on cornstalk decomposition in sand inoculated similarly. The soil suspensions did not

TABLE 3

*Evolution of carbon dioxide from cornstalks in sand with addition of surface soil or surface soil suspension*

SOURCE OF INOCULATION	SOIL ADDITION				SUSPENSION ADDITION			
	Total CO <sub>2</sub> evolved*		Time of peak	Rate of peak	Total CO <sub>2</sub> evolved*		Time of peak	Rate of peak
	mgm.	mgm.	hrs.	mgm./hr.	mgm.	mgm.	hrs.	mgm./hr.
P109-3	528	544	25	4.2	538	587	25	6.0
P55-1	518	547	25	4.7	517	519	25	4.9
P54-1	591	564	25	5.0	598	540	25	5.5
359	610	540	25	5.0	476	516	25	5.2
P8-1	501	491	25	4.0	506	518	24	5.5

\* On basis of 1 gm. cornstalks, 100 gm. sand, and suspension from 5 gm. surface soil for 14 days' incubation.

cause an increase in CO<sub>2</sub> production, and in fact for the first 8 days a slight depression due to the inoculation was suggested. The sterile suspension had no apparent influence either in increasing or in decreasing the decomposition (table 4), whereas the sterile suspension added to P54-10 (table 2) caused a definite decrease in CO<sub>2</sub> production during the first few days of incubation though not at 40 days. There was a decrease in the time elapsing before the peak rate of evolution was reached, and the peak rate itself was increased by surface soil addition to the Fayette subsurface sample, but these effects were not manifest when additions of suspensions were made.

*Evolution of CO<sub>2</sub> from complete and alcohol-extracted soils plus cornstalks to which alcohol extracts of soil had been added*

The introduction of surface soil populations into subsurface soils was not followed by the increase in microbial activity that would have been expected had the introduced population established itself. The data are explainable, however,

on the assumption that there may be microbially produced substances in soil preventing the growth or delaying the development of introduced organisms. Studies on the effect of alcohol extracts of soils on the growth of bacteria and fungi, discussed hereinafter, also point to the same possibility. Almost all of the microbially produced bacteriostatic and bactericidal compounds are only

TABLE 4

*Evolution of carbon dioxide from Fayette subsurface sample plus cornstalks with addition of surface soil or sterile and nonsterile surface soil suspensions*

FORM OF SOIL INOCULUM	CO <sub>2</sub> EVOLVED* DURING INCUBATION					TIME OF PEAK	RATE AT PEAK
	1 day	3 days	8 days	14 days	40 days		
	mgm.	mgm.	mgm.	mgm.	mgm.	hrs.	mgm./hr.
None	6	66	159	222	348		
	4	56	145	203	333	42	1.6
<i>Clarion silt loam (P55-1)</i>							
Soil	19	86	187	244	369		
	13	82	190	251	376	36	1.8
Soil suspension	6	53	137	199	316		
	3	54	137	198	320	42	1.3
Sterile soil suspension	4	61	151	210	331		
	5	60	160	223	342	48	1.5
<i>Fayette silt loam (P109-3)</i>							
Soil	17	87	182	242	375		
	21	90	188	248	383	24	1.8
Soil suspension	4	53	131	188	313		
	4	55	139	203	329	42	1.4
Sterile soil suspension	6	61	159	221	337		
	4	54	145	203	331	48	1.5
<i>Marion silt loam (P8-1)</i>							
Soil	11	80	179	247	389		
	12	76	179	242	376	36	1.8
Soil suspension	6	64	160	221	326		
	6	63	152	214	324	42	1.6
Sterile soil suspension	15	79	172	229	335		
	6	59	143	204	326	36	1.5

\* On basis of 0.5 gm. cornstalks, 50 gm. air-dry P109-9 and suspension from 2.5 gm. surface soil, or 47.5 gm. P109-9 and 2.5 gm. surface soil.

slightly soluble in water but are soluble in organic solvents. Insolubility in water may also be a property of any substances of this type present in soils.

A part of an extensive experiment to test the influence of alcohol extracts of soil on the decomposition of cornstalks in sand or in sand plus complete or alcohol-extracted soil is outlined in table 5. The alcohol extract of 25 gm. of soil was added to 0.5 gm. of cornstalks on top of the sand or extracted soil in

quart milk bottles. The alcohol was evaporated at 70°C., and the last traces were removed by oven-heating at 95°C. for 1 hour. The extracted soil-sand mixture or sand with alcohol extract and cornstalks was sterilized by autoclaving for 1 hour. Complete soil was added to those receiving this addition, all were thoroughly mixed, and sterile  $(\text{NH}_4)_2\text{HPO}_4$  solution together with soil suspension

TABLE 5

*Evolution of carbon dioxide from cornstalks in sand or in sand plus complete or alcohol-extracted soil with and without alcohol extract of soil*

NUMBER	WEIGHT OF SAND	SOURCE OF SOIL*	SOURCE OF SOIL SUSPENSION	SOURCE OF ALCOHOL EXTRACT	CO <sub>2</sub> EVOLVED† DURING INCUBATION					TIME OF PEAK	RATE OF PEAK
					1 day	3 days	8 days	14 days	40 days		
					mgm.	mgm.	mgm.	mgm.	mgm.	hrs.	mgm./hr.
115	50	None	P109-3	None	12*	57	145	215	317	48	1.0
					13	55	133	206	297		
117	50	None	P109-3	P109-3	6	37	94	183	270	48	0.9
					5	41	96	180	252		
127	50	None	P109-9	None	1	50	107	146	207	72	1.1
					3	57	112	154	213		
129	50	None	P109-9	P109-9	4	35	77	110	180	48	0.7
					2	34	84	128	211		
137	50	None	P109-3	P109-9	13	53	118	168	280	48	0.9
					12	46	108	158	262		
121	25	C. P109-3	None	None	48	145	267	381	548	48	2.2
					51	152	280	395	564		
119	25	E. P109-3	P109-3	None	18	122	256	359	540	48	2.4
					17	129	272	390	569		
123	25	C. P109-3	None	P109-3	38	146	289	398	567	48	2.3
					43	147	279	394	565		
133	25	C. P109-9	None	None	1	44	108	153	236	72	1.0
					4	50	113	160	235		
131	25	E. P109-9	P109-9	None	3	28	86	116	157	72	0.7
					2	20	73	110	173		
135	25	C. P109-9	None	P109-9	1	32	96	140	217	72	0.7
					1	30	84	128	200		
141	25	C. P109-9	P109-3	None	9	61	137	201	273	48	1.3
					7	57	127	180	251		
143	25	C. P109-9	P109-3	P109-9	6	49	106	165	245	48	1.1
					5	45	107	172	255		

\* Weight of soil, 25 gm. C. = complete; E. = extracted.

† On basis of 0.5 gm. cornstalks in 50 gm. sand, or 25 gm. sand plus 25 gm. soil. Extract and soil suspension from 25 gm. soil.

inoculum, if required, was added. The soil suspension inoculum represented 25 gm. of soil. The moisture was brought up to the optimum with sterile water. All reasonable care was taken to prevent contamination during the incubation.

Some of the conclusions that may be drawn from the data in table 5 follow:

The Fayette surface soil population (P109-3) was composed quantitatively and qualitatively of organisms better adapted to decompose cornstalks in the sand environment than

was the subsurface population (P109-9), as shown by greater total CO<sub>2</sub> evolution and by the shorter length of time to attain peak CO<sub>2</sub> evolution (numbers 115 and 127).

On the addition of alcohol extracts of either soil to its respective populations in the sand environment, CO<sub>2</sub> evolution was reduced (numbers 117 and 129).

The alcohol extract of P109-9 decreased CO<sub>2</sub> production by the population of P109-3 in sand environment almost as much as did the alcohol extract of its own soil (numbers 137 and 117 compared with 115), though the depression in CO<sub>2</sub> evolution by the alcohol extract of P109-9 on the populations of P109-3 was not apparent during the early part of the incubation period.

Carbon dioxide production from soil P109-3 alcohol-extracted and reinoculated with its own population (number 119) did not differ significantly from that of the complete soil (number 121) except during the first part of the incubation period, when the difference was probably due to the relatively smaller numbers of organisms reintroduced into the extracted soil.

The addition of an alcohol extract of P109-3 to complete P109-3 resulted in no reduction in activity (numbers 123 and 121).

An alcohol extract of the subsurface soil P109-9 reduced the activity of the population of P109-9 in its normal environment (numbers 135 and 133).

The addition of an alcohol extract of P109-9 reduced the activity of the surface soil population when introduced into P109-9 (numbers 143 and 141).

These experiments were interpreted as supporting the view that soils may contain inhibitory substances, the effect of which is to delay or reduce the utilization of added energy material if the population present or introduced is not adapted to the environment containing these substances. In the particular experiments presented here, the Fayette surface soil contained an alcohol-soluble substance which depressed the activity of another population but was without apparent effect on its own population. In the subsurface soil, on the other hand, some effect of the alcohol extract was manifest also on its own population.

#### *Influence of water extracts of soil on soil organisms in vitro*

Substances that may be toxic or inhibitory to organisms in the soil may be soluble in water, in which case they would pervade the soil solution and be distributed throughout the film of water in which soil organisms carry on their activities, or if not water-soluble then they must be produced in the organic residues undergoing decomposition and must have only limited distribution outside of such loci. Of the two, it might be expected that water-soluble substances would have the more potent effect on introduced organisms in preventing or delaying the establishment of a foreign population. In the studies on the inoculation of subsurface soil with surface soil suspensions there was limited evidence of the existence of water-soluble inhibitory substances, in that CO<sub>2</sub> evolution was reduced in the first few hours after addition. Attempts were therefore made to extract from soils water-soluble substances that might affect the growth of microorganisms on plates. The aqueous extracts used in plate counts were prepared by shaking soil with water, centrifuging to remove the soil particles, and concentrating under reduced pressure at 50°C. The addition to Thornton's agar medium of several extracts of this type, representing 2.5 gm. of soil per plate, in only one case resulted in a depression in bacterial numbers developing from a suspension of a Marshall 16-20-inch sample (P54-6). The

autoclaved aqueous extract of the surface Clarion sample P55-1 caused a statistically significant decrease in numbers of bacteria, but an extract of the same soil sterilized by passage through a Berkfeld candle had no effect. Either the inhibitory principle was absorbed during the filtration or else was formed during the heat sterilization.

Aqueous extracts of air-dried surface soils (P55-1 and P8-1) and of fresh incubated Clarion silt loam, representing 2.5 gm. of soil in 10 ml. of broth, were used in pure cultural turbidimetric experiments. Each aqueous extract was incorporated into a medium having the following composition: glucose, 5 gm.; peptone, 5 gm.;  $K_2HPO_4$ , 1 gm.;  $MgSO_4$ , 0.5 gm.;  $FeSO_4$ , trace; water extract of soil, 1000 ml.

The reaction was adjusted to pH 7.6. Normal and soil extract broths were sterilized by passage through Berkfeld candles. The growth of bacteria in this medium was determined by turbidity measurements with the Evelyn photo-electric colorimeter using filter number 520.

The organisms used in these studies were some of the more abundant bacterial species developing on Thornton's agar medium, which had been inoculated with a suspension of the Marshall 16-20-inch sample (P54-6). The bacteria were further selected on the basis of rapidity of growth and development of turbidity in normal glucose-peptone broth. The water extract of air-dried surface soils P8-1 and P55-1 had no influence on the growth of a number of these organisms isolated from P54-6. These results are in accord with the findings of other investigators including Grieg-Smith (2), who noted that air-drying destroyed water-soluble toxic substances present in soil, and Rybalkina (4), who found that the soil solution might exhibit either depressing or stimulating effects on  $CO_2$  production by *Bacillus mycoides* in meat-peptone broth according to the conditions of temperature and moisture prevailing.

Grieg-Smith (2) many years ago observed that incubation at moderate moisture and temperature levels increased the toxicity of soil to *Bacillus prodigiosus*. The water extract of a freshly sampled Clarion surface soil incubated for 16 days at 25°C. was tested for its inhibitory action upon organisms isolated from P54-6. The extract inhibited the growth of only one organism (table 6). The rate of growth of this organism, number 1, was decreased during the first part of the incubation period but not during the latter part.

A water extract of Clarion soil, to which sucrose at the rate of 0.675 gm. per 100 gm. soil had previously been added and which had then been incubated at 25°C. for 1 month at optimum moisture content, caused a slight stimulation of bacterial growth. This stimulation of growth could hardly be due to sugar unutilized by the bacteria during the incubation period. It is, of course, possible that growth stimulants as well as growth inhibitors might be formed in soil by microbial activity.

#### *Influence of alcohol extracts of soil on soil organisms in vitro*

Inasmuch as no clear-cut evidence of the general presence of water-soluble inhibitory substances was obtained, a series of studies was made on the effects

of the presence of alcohol extracts from soils on plate counts of soil bacteria, pure cultural growth of bacteria, and growth of soil fungi. The soils were exhaustively extracted with absolute ethyl alcohol in either a Soxhlet or a Bailey-Walker extractor. Aliquots of the alcohol extract of soil were added to water, and the alcohol was evaporated off. Controls were prepared by adding alcohol to water and treating in the same manner. The water suspensions of the alcohol extracts were diluted with sterile water and added aseptically to equal volumes of sterile double-strength Thornton's agar medium. In all cases the alcohol extract produced a yellow or yellow-green turbidity in water. In a preliminary experiment the alcohol extract of 5 gm. of Clarion surface soil (P55-1) in 10 ml.

TABLE 6

*Growth of bacteria\* in glucose-peptone broth with and without aqueous extract of Clarion surface soil†*

TREATMENT	ORGANISM	GALVANOMETER DIFFERENCE‡					
		20 hours		34 hours		46 hours	
None.....	1	22.5	22.5	25.0	26.5	30.0	29.0
+ extract.....	1	9.5	7.5	19.5	20.0	27.0	28.5
None.....	2	11.0	5.0	24.5	23.0	31.0	28.0
+ extract.....	2	7.5	8.5	28.0	29.0	35.0	35.0
None.....	7	3.5	4.0	7.0	6.0	10.0	8.0
+ extract.....	7	1.0	2.5	6.0	8.0	9.0	12.0
None.....	6	1.5	3.0	5.0	6.0	7.0	8.0
+ extract.....	6	4.5	5.0	7.5	7.5	8.5	9.5
None.....	8	10.5	11.0	19.5	18.0	25.5	24.0
+ extract.....	8	12.5	11.5	19.0	19.5	26.0	25.0

\* Bacteria isolated from Marshall subsurface sample.

† Clarion soil, freshly sampled, incubated 16 days prior to extraction. Extract from 4.2 gm. soil on dry basis per 10 ml. broth.

‡ These figures are the differences in galvanometer readings between inoculated tubes and an uninoculated tube of the same medium or medium plus extract.

of Thornton's agar medium per plate reduced the count of bacteria in a suspension of the Marshall 16-20-inch soil (P54-6) from 91 to 0. In another experiment the alcohol extract from 2 gm. and 0.5 gm. of the same soil reduced the bacterial count from 63 to 1 and from 63 to 21 respectively.

This last experiment showed that even in small quantities of soil it was possible to demonstrate the presence of substances toxic to soil microorganisms. It appeared to be desirable to ascertain the individuality of alcohol extracts of the soil by testing that from one part of the profile on the bacterial counts in a suspension from another horizon of the same profile. The alcohol extract of P54-1 decreased the bacterial counts of soil suspensions from all horizons below



it that were tested, but it did not influence the count of its own soil (table 7). The alcohol extract of P54-6 decreased bacterial counts of P54-12 but not of any other soil. In one instance an alcohol extract increased the bacterial count (extract of P54-9 on P54-6).

The effect of alcohol extract on the pure cultural growth of bacteria was also determined turbidimetrically. By the use of this technique, the growth of organism number 1 was significantly decreased by the extract of 0.5 gm. of P55-1

TABLE 7

*Average numbers of bacteria from soil suspensions of Marshall soil with and without alcohol extracts of the same soil*

SOURCE OF SUSPENSION PLATED	AVERAGE NUMBERS OF BACTERIA†				
	Control	P54-1 extract‡	P54-6 extract‡	P54-9 extract‡	P54-12 extract‡
P54-1	75	71	68	81	70
-6	90	54**	85	117*	98
-9	55	24**	55	51	47
-12	117	61**	97*	114	104

\* Significant by *t* test in comparison with control, beyond 5 per cent level.

\*\* Highly significant by *t* test in comparison with control, beyond 1 per cent level.

† Average of seven plates.

‡ Alcohol extract from 1 gm. of designated soil per plate.

TABLE 8

*Diameter of fungal colonies with and without alcohol extracts of surface soils*

FUNGUS	AVERAGE DIAMETER OF COLONY‡					
	Experiment A		Experiment B		Experiment C	
	Control	Extract from 1 gm. P55-1	Control	Extract from 3 gm. P55-1	Control	Extract from 3 gm. P54-1
	mm.	mm.	mm.	mm.	mm.	mm.
<i>Penicillium humicola</i> .....	21.0	19.0**	23.5	19.8**	23.2	19.7**
<i>Aspergillus sydowi</i> .....	10.7	9.2*	13.7	10.8*	12.8	10.7*
<i>Zygorhynchus vuilleminii</i> .....	78.5	78.7	56.3†	48.5***†	53.0†	55.5†
<i>Sporotrichum pruninosum</i> .....	20.2	18.7**	24.3	20.7**	22.0	19.5**
<i>Monilia humicola</i> .....	22.0	19.0**	27.8	18.8**	28.0	22.5**

\* Significant by *t* test in comparison with control, beyond 5 per cent level.

\*\* Highly significant by *t* test in comparison with control, beyond 1 per cent level.

† Diameter measured on third day of incubation.

‡ Average of three plates after 5 days' incubation.

but not by 0.25 gm. in glucose-peptone broth. The presence of the extract of 1.5 gm. of this soil reduced the amount of growth by half at 36 hours according to turbidimetric measurements.

The alcohol extracts of soils in general did not decrease the number of fungi appearing on bacterial count plates, but the normal variation in numbers of fungi developing on such plates is large. To test the effect of alcohol extracts of soil on growth of fungi in pure culture, plates of Waksman's fungal medium with and without alcohol extract were inoculated with spore suspensions of five

soil fungi, three plates being used per fungus. Inoculation was by means of a loopful of the water suspension of the fungal spores to the center of the solidified medium. The alcohol extract from 3 gm. of P55-1 decreased significantly the growth of all the fungi (table 8), and the extract from 1 gm. of the same soil decreased significantly the growth of all except *Zygorhynchus vuilleminii*. The alcohol extract from 3 gm. of P54-1 decreased the growth of all fungi except *Zygorhynchus vuilleminii*, the growth of which at certain stages appeared to be stimulated by this extract.

#### GENERAL DISCUSSION

The character of the soil population must ordinarily depend to a considerable extent on the nature of the energy material available and on the prevailing environmental conditions. In circumstances when either of these fluctuate, it is probable that the normal microbial inhabitants will be both more varied in type and more versatile in individual abilities than when the energy material is not added sporadically and is relatively uniform in character. The latter is the case in most subsurface horizons, and as a result, there is likely to develop therein a rather stable population characteristic of each particular locus. These differences have been demonstrated by comparison of the rates and amounts of carbon dioxide evolved on addition of a common energy source. Surface populations invariably accomplished rapid and extensive utilization of the added cornstalks, but subsurface populations dealt far less readily with this material despite the presence of an appreciable water-soluble fraction that would ordinarily be considered to be highly available. The introduction of surface populations into subsurface samples was not followed by the substantial increase in activity that might have been expected had the new population supplanted the old. Some factor appeared to be restraining or delaying the rapid onset of decomposition, and it is suggested that this is due to the presence of bacteriostatic or inhibitory agents produced by the indigenous population and, to some extent, probably characteristic of it.

Great interest has been aroused in recent years by the isolation of antibiotic substances of varying degrees of potency produced by soil organisms in the media in which they have been cultured. The subject has been fully reviewed by Waksman (5, 7). Because of the clinical possibilities, almost all the work on these antibiotic agents has been directed to their effect on pathogenic organisms not normally found in soil. Numerous examples of apparently antagonistic relationships between organisms in soil have, however, been described, mostly with fungi, and by workers interested in the control of soil-borne plant pathogens. Some success has followed the attempt to suppress the more specialized root-parasitic pathogens by increasing substantially the saprophytic organisms through addition of particular kinds of crop residues; the effect is believed to be due to the antagonistic action of one or more of the saprophytic species thus favored. These examples, however, are limited in scope, and no well-defined case of antagonism between populations concerned in the normal and essential microbial transformations in soil has been described, nor have the microbiological implications of the formation of antibiotic substances in soil been fully dis-

cussed. Waksman and Woodruff (6) demonstrated the rapid disappearance of coliform organisms introduced into soil, and they extracted from soils an ether-soluble substance that was inhibitory on plates to *B. subtilis* and *Sarcina lutea* but not to *E. coli* (8). The addition of a large amount of actinomycin to soil, however, brought about not a decrease but an increase in the bacterial and fungal populations according to plate counts. They concluded that even though soil organisms may produce in liquid media and in pure culture toxic substances of the nature of actinomycin their action in soil "upon the majority of soil organisms is rather limited."

Any active population consists of a variety of individuals the separate capabilities of which fit together in such a way that the energy material available is utilized efficiently. If the supplies of energy material are relatively constant in composition, as may be the case in certain subsurface soils, there may develop for nutritional reasons a population which does not exhibit a high degree of versatility. In addition, perhaps some members of the population may produce antibiotic substances, in which case the other members of the population would be presumed to be organisms not affected by these particular inhibitors. Introduced organisms would be likely to maintain themselves only if they accomplished as well or better some step in the sequence of transformations by which the energy material is utilized, and were unaffected by any inhibitory substances that might be present. Excessive accumulation of inhibitors is not probable, because this class of substance has been shown to be selective in its action (9). Organisms that are unaffected may well utilize the inhibitor as an energy source, and so tend to offset the suppressive effect of the inhibitor. Whether or not introduced populations may establish themselves then will depend on several factors, among which are (a) their ability to utilize the energy material of the new environment more efficiently than the indigenous population if no inhibitory substances are present, (b) their ability to utilize the energy material more efficiently than the indigenous population even if inhibitory substances repress temporarily or permanently the growth of some of the species introduced, (c) the ability of that part of the population unaffected by inhibitory substances to remove these substances and so permit the development of the organisms at first suppressed.

It is now recognized that the capacity to produce antagonistic substances of varying degrees of potency is widely distributed among soil microorganisms and is not limited to a few specialized forms (8). The corollary of this is that any population in an environment that is nutritionally unvarying will tend to stabilize itself, and because of the inhibitors produced, to resist colonization by other forms. The persistence of a particular organism when the conditions that initially caused it to become dominant no longer prevail, may be affected similarly. The maintenance or disappearance of rhizobia following removal of the legume crop provides a case that might well be investigated from this point of view.

To the picture presented, an additional factor ought to be added which increases the complexity of the problem and about which no information has been sought. Just as there are organisms producing inhibitory substances that

may adversely affect the development of introduced organisms, so may there be organisms producing microbial growth-promoting substances that are essential for the rapid growth of certain forms. In general, soil organisms do not seem especially dependent on vitamins, coenzymes, and the like, but nevertheless some of these substances are required. They may perhaps be supplied more readily from dead microbial tissues than from living cells. Rapid colonization may depend therefore not only on the absence of antibiotic substances but also on the presence of appropriate growth-promoting substances.

#### SUMMARY AND CONCLUSIONS

Subsurface soil samples contain microbiological populations that are smaller, less versatile, and less adaptable than surface soil populations. Introduced plant material is decomposed less rapidly and less extensively. The introduction of surface soil populations by addition of inocula of soil or of soil suspension is not followed by the increase in activity that would be expected. The same inocula in sand accomplish rapid decomposition of plant material. Some factor in the subsurface samples prevents the rapid development of the introduced organisms. Evidence is given supporting the view that antibiotic or inhibitory substances are responsible for this effect, and the theory is presented that these substances are of microbial origin.

Aqueous extracts of soil do not adversely affect the growth of soil bacteria *in vitro*, but alcohol extracts may reduce the activity of the organisms in soil, the development of bacteria in liquid culture or on plates, and the rate of growth of fungi on plates.

The factors affecting the development of subsurface soil populations are discussed. Because the nutritional conditions vary little, and because of the presence of inhibitory agents, subsurface populations tend to stabilize themselves and to resist displacement or colonization by other introduced forms.

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# AZOTOBACTER CHROOCOCCUM AND ITS RELATIONSHIP TO ACCESSORY GROWTH FACTORS

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That organic constituents which may stimulate but are not essential for the growth and metabolism of *Azotobacter chroococcum* occur in soil appears evident from numerous experiments. For example, ashed soil extract usually increases nitrogen fixation less than does unashed soil extract. The potency of the stimulant varies with the specific soil from which the extract was obtained and with the microorganisms on which it is tested. It is most efficient when obtained from highly fertile calcareous soil and least efficient when obtained from some alkali soils. Extracts of grains and plants also have this characteristic (3).

Greaves, Jones, and Anderson (5) grew *A. chroococcum* in a molybdenum-free basal medium containing certain amino acids. Only six of the fifteen amino acids tested materially increased nitrogen fixation, and even these gave no evidence of being essential. Serum albumin or casein added to the basal medium increased nitrogen fixation to a greater extent than did the amino acids. Casein in some cases increased fixation over 200 per cent. Carefully dialyzed casein also increased fixation, but not to the extent of the undialyzed.

Hervey and Greaves (6) found that heat-killed suspensions of *Colpoda* when inoculated into *A. chroococcum* cultures in small quantities stimulated nitrogen fixation to the same extent as did living protozoan cells. The stimulant is not destroyed at a temperature of 65° C. for 30 minutes, but is inactivated by heating 2½ hours at 10 pounds' pressure. It need be present only in minute quantities. Seitz filtrates of the substance have no stimulating effect, indicating that the substance may be an organic colloid. The stimulation is exerted even though the *A. chroococcum* is cultured in a medium containing molybdenum.

Greaves and Bracken (4) determined the nitrogen-fixing powers of numerous alfalfa and virgin soils in Cache and Juab Counties by inoculating the samples into a standard liquid medium. Statistical analysis showed a highly significant difference in favor of alfalfa soil in the first, second, and third foot depths. Consequently the conclusion was drawn that alfalfa, when grown on soil, either increases the number or the physiological efficiency of the nitrogen-fixing microflora of the soil. It is not clear from the data presented whether the increased activity was due to a better source of carbonaceous material, the draining from the soil of its soluble nitrogen, the physical action of the alfalfa plants upon the soil making it better suited to nonsymbiotic nitrogen fixers, the excreting of organic substances that provide a source of energy for the bacteria, or the production of accessory food substances that are unessential yet increase nitrogen fixation.

Greenhouse experiments (4) on soil from a permanently fallow plot at the Nephi Dry-Land Substation (Juab County) mixed with varying quantities of

finely ground legume and nonlegume residues kept bare showed that the alfalfa residues increased the nitrogen fixation of the soil 48 per cent over that of similar soils which had received other legume residues, and the annual gain in nitrogen was 15 pounds per acre more than that in soils which had received no plant residues.

Numerous field and laboratory tests have demonstrated that both nitrogen fixation and nitrification are more active in soils producing alfalfa than in similar soils not producing alfalfa (4). This difference is perceptible some time after the soil has been planted to other crops.

There is a greater microbial population in the vicinity of plant roots than elsewhere in the same soil, and this is occasionally fifty times as great in the vicinity of legumes as it is in the vicinity of nonlegumes (22). These differences have been ascribed to: (a) the deposition of the epithelial cells of the growing roots and the dead parts of the roots; (b) excretion by the roots of readily assimilable organic substances; (c) excretions by the roots of accessory food substances; (d) excretions of organic acids and carbon dioxide, which change the reaction of the soil solution and the solubility of certain soil constituents; (e) modification of the structure of the soil, thus making it a more favorable medium for the growth of microorganisms. Kostychev (11) believes it impossible that the enormous number of living microorganisms in the rhizosphere are dependent upon humus and remains of dead roots as a source of food and energy. Starkey (22) writes: "The extent of the effects of plants upon the soil organisms is not determined by the size of the different plants or by the extent of root development, but may be associated with some characteristics of the physiology of the plant, particularly as regards quality and quantity of root excretions." Timonin (23) found that flax when grown under aseptic conditions excretes significant quantities of thiamin and biotin, which he believes may explain the accumulation of microorganisms in the rhizosphere of growing plants.

It therefore seems permissible to conclude that alfalfa stimulates nonsymbiotic nitrogen fixation in the soil and that this stimulation is not the result of a low soluble-nitrogen content, which would force the nonsymbiotic organisms to become more efficient nitrogen fixers, for stimulation continues after the legume is removed and occurs if legume residues are added to the soil.

To obtain more specific information on this subject two sets of investigations were conducted, in which were determined, first, the quantity of nitrogen fixed by *A. chroococcum* in the presence and in the absence of various accessory growth factors, and second, the production of accessory growth factors by *A. chroococcum* when grown on media to which no accessory growth factors were added.

#### EXPERIMENTAL

The influence of accessory growth factors on *A. chroococcum* was determined by growing this organism in Greaves' medium (3) without molybdenum and with 1 p.p.m. The method was as follows: Media were distributed in 100-ml. portions into 500-ml. Erlenmeyer flasks and autoclaved at 120°C. for 15 minutes. The various accessory growth factors and inoculum were then added, in-

cubated for 15 days at 28°C., and total nitrogen was determined by the Kjeldahl method. The heat-stable accessory growth factors were added in the various concentrations to the flasks of media and sterilized at 120°C. for 15 minutes. Heat-labile substances were sterilized by filtration, and the filtrate was added under aseptic conditions.

The methods used to determine the ability of *A. chroococcum* to synthesize the accessory growth products were those of the Texas University workers (28). The test organisms with the exception of *A. chroococcum* were from the American Type Culture collection. The *A. chroococcum* filtrate was prepared by seeding *A. chroococcum* into Greaves' medium to which had been added 1 p.p.m. molybdenum. The contents of ten flasks were mixed after 15 days' incubation, benzene was added, and the cultures were allowed to autolyze for 24 hours. They were adjusted to pH 4.7 and steamed for 30 minutes. The clear filtrate, referred to as "Azotobacter filtrate," was used in the various experiments.

The chemicals used in the study were of the highest purity obtainable.<sup>1</sup> The culture of *A. chroococcum* was isolated from the Greenville Experimental Farm soil and had been regularly transferred in pure culture for 2 years.

#### *Effect of growth factors on nitrogen fixation*

The gains in nitrogen due to the specific accessory growth factors are given in table 1. Yeast filtrate factor at a concentration of 0.5 ml. in 100 ml. of medium in the absence of molybdenum increased the quantity of nitrogen fixed from 3.5 to 12.4 mgm. The stimulation was probably caused by traces of molybdenum carried by the filtrate factor, as there was no increase in the presence of molybdenum. This also is true of thiamin, which slightly increased nitrogen fixation in the absence but not in the presence of molybdenum. Ascorbic acid was the only compound tested which increased nitrogen fixation in the presence of molybdenum, and in this case the increase was so small that the vitamin should be considered a stimulant and not a required constituent. To determine whether the effect of ascorbic acid might be due to its reducing effects, various reducing agents were used. These were found to be either toxic or without effect. Ascorbic acid may act as a readily available source of energy, and the small increase in the nitrogen fixation by *A. chroococcum* may be the result of this factor. Hence it is permissible to conclude that none of the compounds listed in table 1 is essential for the normal growth and metabolism of *A. chroococcum*. Thiamin, riboflavin, and ascorbic acid stimulated slightly in some concentrations but no evidence was obtained that any of these is essential or materially increases *A. chroococcum* metabolism.

#### *Synthesis of growth factors*

Microbiological methods were used to determine whether some of the accessory growth factors considered are synthesized by *A. chroococcum* and if so in what quantities.

<sup>1</sup> We are indebted to Agnes Fay Morgan, of the University of California, for supplying the filtrate factor, and to R. J. Williams for supplying the folic acid.



The riboflavin content of the *A. chroococcum* filtrate was determined according to the method of Snell and co-workers (28, pp. 11-13). Assays were made at different concentration levels. Only consistent results were used in the averages, which together with those given by Elvehjem (2) for brewers' yeast, skim milk powder, and brewers' grain are given in table 2. These results indicate that 100 ml. of the *A. chroococcum* filtrate carries 1.6 times as much riboflavin as 1 gm. of brewers' grain, 0.41 times as much as 1 gm. of skim milk powder, and 0.11

TABLE 1

*Gain in nitrogen by Azotobacter chroococcum when cultured in media containing various accessory growth factors*

ACCESSORY GROWTH FACTOR	CONCENTRATIONS TESTED	GAIN IN NITROGEN DUE TO ACCESSORY GROWTH FACTOR	
		Without molybdenum	With molybdenum
	<i>p.p.m.</i>		
Biotin.....	0.001 to 0.1	0	0
Carotene.....	0.1 to 100	0	0
Colchicine.....	1	....	0
Ergosterol.....	0.1 to 100	0	....
Filtrate factor.....	0.1 to 1*	+	0
Indole-3-acetic acid.....	1 to 150†	0	0
Indole butyric acid.....	1 to 100	0	0
Indole-3-propionic acid.....	1 to 100	0	0
γ (Indole 3)n-butyric acid.....	1 to 100	0	0
Inositol.....	2.5 to 50	0	0
Nicotinamide.....	0.5 to 10	0	0
Nicotinic acid.....	0.1 to 100	0	0
Pantothenic acid.....	0.05 to 1	0	0
Phenylacetic acid.....	1 to 150	0	0
Phenylpropionic acid.....	1 to 150	0	0
Picoline.....	10 to 100	0	0
Pimelic acid.....	0.1 to 100	0	0
Thiamin.....	0.1 to 100	+	0
Riboflavin.....	0.1 to 100	0	....
Pyridoxin.....	0.05 to 10	0	0
Ascorbic acid.....	1 to 100	+	+

\* MI.

† Toxic at 20 p.p.m.

+ Stimulates.

times as much as brewers' yeast. The relationship is quite different, however, if the substances are compared on the dry basis. The authors have found the dry weight of *A. chroococcum* cells in 100 ml. of the medium used for the culture of these cells for the riboflavin assay, at the end of 15 days, to be 0.2 gm. On the assumption that the riboflavin is proportional to the number of the living cells, 1 gm. of *A. chroococcum* cells would be 7.8 times richer in riboflavin than is brewers' yeast, twice as rich as skim milk powder, and one half as rich as brewers' grain.

The pantothenic acid content of *A. chroococcum* filtrate was determined by the method of Pennington and co-workers (28, pp. 14-17). The average results for 100 ml. of *A. chroococcum* filtrate together with those reported by Pennington and co-workers for rice bran, dried yeast, egg yolk, and egg are given in table 2. Rice bran and some dried yeast carry more pantothenic acid than does 100 ml. of *A. chroococcum* extract, but if all the pantothenic acid is assumed to be contained within the bacterial cell, 1 gm. dry weight of *A. chroococcum* cells carries 170  $\gamma$  pantothenic acid. Hence it is possible that *A. chroococcum* cells are richer in pantothenic acid than is dried yeast or egg and compare favorably with rice bran.

TABLE 2

*Vitamin B complex found in Azotobacter chroococcum filtrate and other substances*

SUBSTANCE	VITAMIN CONTENT	
	$\mu\text{gm.}/\text{gm.}$	$\mu\text{gm.}/100\text{ ml.}$
<i>Riboflavin</i>		
Brewers' yeast.....	62.5	
Skim milk powder.....	17.0	
Brewers' grain.....	4.5	
<i>A. chroococcum</i> filtrate.....		7
<i>Pantothenic acid</i>		
Rice bran extract.....	161-298	
Dried yeast.....	20-80	
Egg yolk.....	47	
Egg.....	8-32	
<i>A. chroococcum</i> filtrate.....		34
<i>Nicotinic acid</i>		
Corn meal.....	6.3-10.3	
Milk, fresh.....	0.84	
Yeast extract.....	665	
<i>A. chroococcum</i> filtrate.....		318

The nicotinic acid content of *A. chroococcum* filtrate was determined by the method of Snell and Wright (28, pp. 22-23). The assays were made at different concentration levels, and in case of satisfactory agreements, results were averaged. The average results for the filtrate and the values reported by Snell and Wright for corn meal, fresh milk, and yeast extract are given in table 2. The nicotinic acid content of *A. chroococcum* filtrate is far greater than that of corn meal or fresh milk and nearly one half that of yeast extract. The *Azotobacter* cells therefore appear to be considerably richer in nicotinic acid than yeast cells. The ease with which *A. chroococcum* may be cultured, raises the question: May *A. chroococcum* be cultured as a source of nicotinic acid? It is an organism easily cultured on a synthetic medium and actively synthesizes nicotinic acid.

The thiamin content of *A. chroococcum* filtrate was determined by the method of Williams and co-workers (28, pp. 31-34). The results obtained for the dif-

ferent assay levels, given in table 3, show rather wide variations. The average of 14  $\gamma$  per 100 ml. of the filtrate is, however, a close approximation of the thiamin

TABLE 3

*Vitamin B complex of Azotobacter chroococcum filtrate as determined at different assay levels*

<i>A. chroococcum</i> FILTRATE PER ASSAY TUBE	VITAMIN CONTENT OF FILTRATE	
	In assay tube	Per 100 ml.
	$\gamma$	$\gamma$
<i>ml.</i>	<i>Thiamin</i>	
0.009	0.0012	13.3
0.03	0.0046	15.3
0.05	0.0054	10.8
0.07	0.010	14.3
0.09	0.0144	16.0
	<i>Inositol</i>	
0.3	0.05	16.7
0.5	0.07	14.0
0.7	0.08	11.0
0.9	0.09	10.0
1.1	0.09	8.2
1.3	0.13	10.0
1.5	0.16	10.7
	<i>Pyridoxin</i>	
0.0001	0.0002	200
0.0005	0.0002	40
0.001	0.0015	150
0.002	0.0068	340
0.004	0.01	250
0.006	0.01	167
0.008	0.0064	80
0.01	0.0064	64
	<i>Biotin</i>	
0.0002	22	11.0
0.0003	35	11.7
0.0004	48	12.0
0.0005	56	11.2
0.0006	64	10.7
0.0007	67	9.6
0.0008	69	8.6
0.0009	72	8.0

content. It is evident that *A. chroococcum* readily synthesizes thiamin, and according to these results its cells may be considerably richer in thiamin than are yeast cells or meats. They compare favorably with wheat germ. The culture

medium upon which the microorganisms were grown was carefully freed of thiamin; hence the compound has been synthesized and not concentrated by the cell, as is the case with some microorganisms. This activity is not peculiar to *A. chroococcum*, however, for thiamin has been shown to be synthesized by the organisms of such biologically separated genera as *Torula*, *Oospora*, *Actinomyces*, and four genera of *Eubacteriales* (20).

The inositol content of *A. chroococcum* filtrate was determined by a modification of the method of Williams and co-workers (28, pp. 27-30). The results obtained for the different assay levels are given in table 3. No inositol was obtained when *A. chroococcum* filtrate was used in concentrations between 0.01 and 0.1 ml.; hence the medium was concentrated to one fourth its original volume and 0.5 ml. added to each test tube. Quantities of inositol needed for the controls and for the *A. chroococcum* filtrate were added, and the volume when required was made up to 2 ml. with sterile distilled water. This method permitted the testing of 1.5 ml. of *A. chroococcum* filtrate. A slight stimulation of the test organism resulted with the higher concentrations. The question may be raised, therefore, whether this is due to inositol or to some other accessory growth factor supplied by the filtrate. The agreement between 0.7 and 1.5 ml. of the filtrate is fairly good. The average inositol content of 100 ml. of *A. chroococcum* filtrate is 11.5  $\gamma$ ; therefore 1 gm. of *A. chroococcum* may contain approximately 58  $\gamma$  inositol. This value is low when compared with the inositol content of muscle and brain tissue, but it is evident that this microorganism synthesizes inositol.

The pyridoxin content of the *A. chroococcum* filtrate was determined by the method of Williams and co-workers (28, pp. 14-17). The results, given in table 3, are averages of three determinations; yet they are erratic and cannot be taken as quantitative. The trend, however, is slightly upward in the case of both the controls and the *A. chroococcum* filtrate. The results strongly suggest that pyridoxin is synthesized by *A. chroococcum*. Other tests indicated that the filtrate became toxic to this particular strain of yeast beginning at a concentration of 0.03 ml. Whether this toxicity is due to pyridoxin or to other synthetic or analytic products is not evident from the results.

The biotin content of *A. chroococcum* filtrate was determined by the method of Snell and co-workers (22, pp. 18-21). As shown by the results in table 3, the agreements in the lower dilutions are good. The data demonstrate that *A. chroococcum* synthesizes biotin, and the concentration of biotin in dry *A. chroococcum* cells compares favorably with that in animal tissues. West and Wilson (26) concluded from a comparison of the growth effects of concentrations of biotin and coenzyme R on yeast and *Rhizobium* that biotin and coenzyme R are probably identical. The evidence is that biotin is required generally by the *Clostridia* (18); is required by the root nodule bacterium *Rhizobium trifolii* (2), by *Lactobacillus arabinosus*, and by *Lactobacillus casei* (21); and is a growth factor for *H. hemolyticus* (7). Landy and Dicken (12) have demonstrated that many bacterial species cultured in synthetic biotin-free media synthesize biotin in variable amounts, suggesting that biotin may be of widespread and fundamental importance.

## DISCUSSION

Azotobacter can synthesize its protoplasm from inorganic nitrogen, provided a suitable form of organic carbon together with required mineral constituents is available. Findings that suggest the need for unknown accessory food substances have, however, appeared sporadically in the literature. The work reported herein warrants the conclusion that the following compounds are not essential for normal growth and metabolism of *A. chroococcum*: biotin, carotene, colchicine, ergosterol, filtrate factor, indole-3-acetic acid, indole butyric acid,  $\gamma$  (indole 3) n-butyric acid, indole-3-propionic acid, inositol, nicotinamide, nicotinic acid, pantothenic acid, phenylacetic acid, phenylpropionic acid, picoline, pimelic acid, thiamin, riboflavin, pyridoxin, and ascorbic acid. Hence *A. chroococcum* differs widely from the following microorganisms, which must be supplied with one or more of these compounds: *H. influenzae* and related types, propionic and lactic acid bacteria, staphylococci, diphtheria bacilli, dysentery bacilli, brucella, *Proteus vulgaris*, and probably *Cl. tetani*, certain of the true fungi including some of the yeasts, and certain protozoa (9).

Apparently, the better growth of *A. chroococcum* cultured on legume residues in comparison with that of the same species cultured on nonlegume residues is not the result of any known accessory growth factor (4). Linford (14), after careful microscopical examination of the microflora associated with plant roots, concluded that the early concentration of microorganisms in the rhizosphere is not dependent upon the destruction and utilization of senescent and dead root cap cells, root hairs, and cortical tissues but that apparently the microorganisms utilize nutrients that diffuse out of the active root cells or are otherwise beneficial from a local alteration of the soil environment under the influence of the roots. If Timonin's (23) suggestion that the accumulation of microorganisms in the rhizosphere of the growing plants is due to the excretion of thiamin and other accessory growth-promoting substances is correct, these organisms must lack the synthetic ability of *A. chroococcum*.

It is possible that there are unknown accessory growth factors, as *A. chroococcum* is stimulated by unwashed casein and minute quantities of heat-killed protozoa. In these cases the quantity added to the medium would be too minute to render available plant nutrients, as Lind and Wilson (13) found to occur when *A. chroococcum* was grown in conjunction with an aerobic spore-bearing contaminant.

That *A. chroococcum* apparently uses some accessory growth factors in its metabolism is evident from the fact that it actively synthesizes biotin, inositol, nicotinic acid, pantothenic acid, pyridoxin, riboflavin, and thiamin. The ability to synthesize these compounds is not peculiar to *A. chroococcum*, for approximately 60 species of bacteria have been found to synthesize riboflavin or a substance capable of replacing riboflavin as an essential growth factor for *L. casei* (24). The amount found to be synthesized varied from 0.02 to 3.6 per ml. of bacterial culture, and it is suggested that the beneficial effect observed by some workers when certain microorganisms grow in symbiosis with others

may be the result of this factor. The specific function of riboflavin to bacteria is not fully understood, but inasmuch as the fermentative ability of yeast and *Azotobacter* is similar, insight into its function may be gained from an examination of yeast metabolism.

Warburg and Christian (25), in 1932, isolated from yeast a flavoprotein which, in acid solution, was split into a protein and a riboflavin phosphate. Cozymase I of Euler and cozymase II of Warburg and Christian are adenylic acid nucleotides of nicotinic acid and nicotinamide and are important  $H_2$ -carriers capable of passing hydrogen to flavoproteins. Hence the enzymes into which riboflavin and nicotinic acid enter, catalyze the dissimilation of hexose phosphate. Kligler and Grossowicz (8) demonstrated that some microorganisms which required nicotinic acid, when grown in a carbohydrate-containing medium, metabolize normally in a medium free of nicotinic acid.

Nicotinic acid and nicotinamide do not always produce equivalent growth-promoting effects on microorganisms (10); hence it has been contended that nicotinamide is concerned in cellular oxidation in some way other than in the formation of pyridine nucleotides (19).

Thiamin functions in the economy of a wide variety of microorganisms, and according to Williams (29, p. 156) one can scarcely regard it otherwise than as "one of nature's earlier and more fundamental inventions in the process of evolving life."

Lohmann and Schuster (15) in 1937 found in yeast a diphosphate ester of thiamin that functions as the coenzyme cocarboxylase for the enzyme carboxylase, which is concerned in the conversion of pyruvic acid into carbon dioxide and acetaldehyde. The same year Lipmann showed that the oxidation-decarboxylation of pyruvic acid to acetic acid and carbon dioxide, or its dismutation by alkaline-washed lactic acid bacteria into lactic acid, acetic acid, and carbon dioxide, was catalyzed by cocarboxylase and not by free thiamin. Banga and co-workers (17) in 1939 presented final proof that in the form of its pyrophosphate, thiamin is necessary for the oxidative removal of pyruvic acid and, indirectly, of lactic acid in normal carbohydrate metabolism. Hence it is permissible to conclude that thiamin, like riboflavin and nicotinic acid, plays a vital role in the carbohydrate dissimilation of *A. chroococcum*.

Cytochrome C, which plays an important part in conjunction with cozymase I and II in carbohydrate dissimilation, has within it an unknown group, which Elvehjem (1) suggests may be related to biotin.

Inositol is important in the growth and budding of yeast, and it may play a similar role in *Azotobacter* multiplication. The two remaining accessory food substances, pyridoxin and pantothenic acid, are intimately associated with cell proteins, and they probably play a role in some enzymic system.

The authors have demonstrated that *A. chroococcum* actively synthesizes accessory growth factors, and the quantity found in these cells compares favorably with that found by other workers in yeast cells. It should be borne in mind, however, that the quantity synthesized may vary with the species and possibly with the strain, for Wilson and Wilson (30) have found that rhizobia

may be divided into three groups based upon their biotin requirements: (a) Most strains in the absence of biotin grow very poorly and reach a population of about one tenth the maximum, though continuous serial transfer is possible; (b) a few strains attain virtually maximum growth in its absence; (c) a few strains are unable to grow unless biotin is supplied. Such a grouping may imply either that some strains and not others have the ability to synthesize biotin, or that some strains require it in their metabolism whereas others do not. In either case it demonstrates the wide variation that may occur in nearly related microorganisms.

From the accessory growth factors synthesized by *A. chroococcum* and from the postulated functions of these factors, we may assume that the general catabolic carbohydrate transformations of this species are similar to those of yeast. It must be remembered, however, that the anabolic carbohydrate transformations may be the reverse of these transformations, for O'Kane (16) has found that cells of *Thiobacillus thiooxidans* grown on a completely inorganic medium contain nicotinic acid, pantothenic acid, biotin, riboflavin, and pyridoxin.

The discovery that *A. chroococcum* readily synthesizes the accessory growth factors suggests the use of this organism as a source of these compounds. The organism is readily cultured on a synthetic medium; hence, the accessory growth factors may be more easily purified than when produced in more complex media. It is also possible that *A. chroococcum* together with other soil microorganisms may furnish accessory growth factors to higher plants when grown in the presence of microorganisms which possess the ability to synthesize such factors, and this may explain why some investigators have found these accessory growth factors to be nonessential to higher plants, whereas other investigators have concluded that they are essential (27). It is also possible that the quantities of the vitamin B complex present in plants may be related to the microflora of the soil. These phases of the problem are being studied at the present time.

#### SUMMARY

Although there appears sporadically throughout the literature of the past, implication that *Azotobacter chroococcum* requires certain accessory food substances, the present work demonstrates that the following compounds are not needed in media for the normal growth and metabolism of this organism: ascorbic acid, biotin, carotene, colchicine, ergosterol, filtrate factor, indole-3-acetic acid, indole butyric acid, indole-3-propionic acid,  $\gamma$  (indole 3) n-butyric acid, inositol, nicotinamide, nicotinic acid, pantothenic acid, picoline, pimelic acid, thiamin, riboflavin, and pyridoxin. Thiamin, riboflavin, and ascorbic acid stimulated slightly in some concentrations, but no evidence was obtained that any of these compounds are essential or materially increase *A. chroococcum* metabolism.

*Azotobacter chroococcum* when grown in a synthetic medium free from accessory food factors synthesized biotin, inositol, nicotinic acid, pantothenic acid, pyridoxin, riboflavin, and thiamin. The quantity synthesized compares favorably with the quantities found in other plant tissues including yeast. These compounds apparently enter into the synthesis of the bacterial enzymes.

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## SOME FACTORS INFLUENCING AGGREGATION OF CLAYPAN SOILS

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The stability of the aggregates of soil and the factors influencing it have had increased attention during the last few years. Though several factors have been shown to influence aggregation, their relative importance still remains somewhat obscure. In order to evaluate more accurately the relative effectiveness of a few factors, particularly the crop factor, that might be important influences, the aggregation of the surface soil of certain of the fertility plots on the Moran Experimental Field in Allen County, Kansas, was studied.

### AREA STUDIED

The soils of the experimental area were of the Woodson and the Parsons series, both claypans developed under prairie vegetation. One part of the study was made on soils taken from plots which had been given different fertilizer treatments and on which crops had been grown in rotation; the other was made on soils from areas on which grass had grown for various lengths of time. Thus it was possible to assemble comparisons of the influences of crops and soil treatments on soil aggregation.

The field experiment on which the study was made consisted of six series, each of which was devoted to one crop of a rotation, Atlas sorgo, corn, soybeans in 21-inch rows, oats, red clover, and alfalfa. Each series was subdivided into twelve 1/10-acre plots on which were applied different lime, manure, and fertilizer treatments. One plot in each series was given no soil treatment, and on it nonlegumes were substituted for the legume crops in the rotation. The substitutions were Club sorghum, Sudan grass, and a tame grass mixture for soybeans, red clover, and alfalfa, respectively. Alfalfa (or grass on the nonlegume plot) was allowed to grow on a given series for an interval of 5 years unless failure to maintain a stand shortened the period. During this 5-year interval the other crops were rotated on the remaining five series. Alfalfa (or grass on the nonlegume plot) has been grown on series A, C, F, and B in that order since the start of the experiment. Series D was in alfalfa in 1940, leaving series E as the only block on which the crop has not grown.

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Two of the plots on each series were selected for study because of the wide difference in treatment: one received lime, manure, and superphosphate and was included in the legume rotation; the other was the untreated plot in the nonlegume rotation.

The red clover seeding failed in 1939; therefore, closely drilled soybeans were substituted in 1940. At the time the samples were taken, red clover was growing in the oat stubble in the legume rotation, and weeds were growing in the stubble in the nonlegume rotation. On the treated plots, manure was applied every fifth year, at the rate of 8 tons per acre, preceding the corn crop. Superphosphate was applied annually and at different rates for the different crops. Lime at the rate of 3 tons per acre was applied at the beginning of the experiment. Series D received an additional ton per acre prior to the seeding of alfalfa.

For the soils that had been under grass for various lengths of time without cultivation and with different intensity of use, three 1/10-acre grass areas were sampled. One of these was an untreated plot on the experimental field on which a tame grass mixture had grown since 1930 except for the years 1933 and 1934. The second was a native grass meadow across the road from the field site. The third was a somewhat overgrazed native pasture adjacent to the meadow.

#### METHODS

Nine randomized samples were taken from each plot. The plots were stratified crosswise into thirds. Each third was subdivided into 20 equal areas, from which the three areas to be sampled were selected at random by drawing numbers. The sample was taken from the point where an object tossed onto the area came to rest. Samples were taken to a depth of  $6\frac{1}{2}$  inches by means of a spade, care being taken to prevent mechanical disruption of the aggregates by the spade. The samples were put through a half-inch screen and allowed to air-dry. After thorough mixing, a portion of each sample was removed for aggregate analyses. The remaining portions of the three samples from each third of the plot were mixed and prepared for chemical analyses.

All samples were taken on September 20 and 21, 1940. Though the moisture contents were not identical, it is believed that differences were due chiefly to the crops, since no precipitation fell during or for some time before the sampling period. Moisture contents were all near the calculated wilting point.

Aggregate analyses, in duplicate, were made by wet-sieving samples containing the equivalent of 100 gm. of oven-dry soil. A nest of three U. S. standard sieves, viz., the 4.0, 2.0, and 0.105 mm. on which the soil had been placed, was operated mechanically for 15 minutes in distilled water through a vertical distance of about 2 inches at the rate of 30 strokes per minute. Results are reported as the percentage of the original sample coarser than 0.105 mm.

Only the results of the original duplicate aggregate analyses were used in the summary, despite apparent limited agreement between a few of the duplicate readings. Though repeat analyses were made on those samples the duplicate readings of which did not conform to a previously conceived standard of perfection, statistical analyses showed that the resulting re-runs made no real dif-

ference in the interpretation of results and made the analysis of data more difficult.

Nitrogen analyses were made according to the Gunning-Hibbard method modified to include distillation of the ammonia into boric acid solution. Organic carbon determination was made by the Schollenberger method as modified by Allison (2). The lime requirement measurement was by the Jones method as modified by Bayer (3).

TABLE 1

*Effect of crop on the percentage of water-stable aggregates and the relationship of aggregation to certain soil factors*

SERIES	CROP—1940	YIELD PER ACRE	AGGREGATES COARSER THAN 0.105 MM. ( $N = 18$ )	CHEMICAL NATURE OF SOILS ( $N = 6$ )			
				Nitrogen	Organic carbon	Carbon Nitrogen ratio	Lime ( $\text{CaCO}_3$ ) requirement
		tons	per cent	per cent	per cent		pounds
<i>Lime, manure, and superphosphate plus legumes</i>							
A	Atlas sorgo	8.59	48.9	0.143	1.79	12.5	2016
B	Corn	35.30*	53.4	0.143	1.76	12.3	1163
C	Oats and red clover	1.28	52.4	0.144	1.89	13.1	1387
D	Alfalfa (3 years)	4.03	66.9	0.127	1.69	13.3	1664
E	Soybeans (rows)	2.84	39.1	0.126	1.69	13.4	2368
F	Soybeans (drilled)	2.80	50.4	0.146	1.89	12.9	2283
<i>Untreated, no legume</i>							
A	Atlas sorgo	6.40	50.5	0.142	1.86	13.1	4587
B	Corn	46.00*	55.8	0.136	1.82	13.4	4501
C	Oats	0.57	49.5	0.122	1.55	12.7	4128
D	Tame grass mixture (3 years)	1.06	57.8	0.122	1.58	13.0	3989
E	Club sorghum	0.49	38.8	0.114	1.53	13.4	2883
F	Sudan grass	1.35	46.8	0.126	1.70	13.5	4267
Correlation coefficient ( $r$ ) all plots ( $N = 36$ ), between aggregation and chemical factor of soil†...				0.188	0.291	-0.041	-0.221

\* Bushels.

† Value of  $r$  necessary for 5 per cent level = 0.325.

## EXPERIMENTAL RESULTS AND DISCUSSION

### *Soils under treatment with crops in rotation*

A summary of the results of the aggregate studies for the cultivated plots is given in table 1. Also given are the crop yields for 1940, the percentages of nitrogen and organic carbon in the soils, the carbon-nitrogen ratio, the lime requirement of the soils, and the correlation coefficients between aggregation and other soil factors.

A statistical summary of the aggregation data is given in table 2. The mean

squares for the random samples in the same third of the plot, which represents the soil variability, is the estimate of error against which the other mean squares are tested. The crop difference is highly significant. On this point the results are in agreement with many that have been reported by other investigators (1, 7, 8, 11, 13, 21, 23). Neither treatment nor the interaction of crop and treatment showed statistically significant differences. Thus, manure, lime, and superphosphate and legume in the rotation had no permanent effect on aggregation either directly or through interaction with the crop. The average percentages of the soil coarser than 0.105 mm. of the aggregate data in table 1 for Atlas sorgo, corn, and oats were 51.6 and 51.9 respectively, for the treated and the untreated plots.

The mean square for thirds in the same plot is so nearly the same as that for random samples as to indicate that in respect to total aggregates greater than 0.105 mm. there is no trend or progressive difference from one end of the plot to the other. The mean square for duplicates, which represents the variability

TABLE 2  
*Results of statistical analysis of data in table 1*

	D/F	SUMS OF SQUARES	MEAN SQUARES
Treatment.....	1	217.8038	217.8038
Crop.....	5	10596.3236	2119.2647**
Crop X treatment.....	5	795.7509	159.1502
Thirds in the same plot.....	24	1905.0244	79.3852
Random samples in the same third of plot....	72	5247.8267	72.8865
Duplicates.....	108	1963.2850	18.1786

\*\* Highly significant.

of the laboratory technic, is small as compared to the mean square for random samples in the same third. This indicated that the laboratory technic was sufficiently refined for the variation found in the experiment.

The corn plot in the treated series received 8 tons of manure to the acre during the early spring of 1940. Even if it were assumed that this application had an early favorable effect on aggregation, it is evident that its influence was of short duration, for at the time of sampling, the difference between the corn plots in the treated and the untreated group was slight. Similarly, Bertramson and Rhoades (5) found that manure additions equivalent to  $4\frac{1}{2}$  tons per acre annually over a period of years had no measurable effect on aggregation. Likewise, Browning (6) and Peel *et al.* (17) found that the addition of cured legume hay did not appreciably change aggregation of the soils in their experiments.

The favorable effect of the alfalfa on soil aggregation was highly significant, as indicated in table 1, but it appeared to be of short duration.

The influence of row spacing of soybeans on the effect of this crop on aggregation appears to be worthy of note. The 21-inch spacing resulted in a lower degree of aggregation than did the 7-inch spacing.

The pronounced unfavorable influence of the Club sorghum on aggregation seemed to be at variance with the results obtained with both Atlas sorgho and corn. The yield differences offered a possible explanation. The exceedingly low yield of Club sorghum indicates a soil condition approaching that of summer fallow, which was shown by Metzger and Hide (13) to reduce the degree of aggregation. In contrast to this, both Atlas sorgho and corn produced relatively large yields in 1940.

Though the tame grass had a favorable effect on aggregation, its influence was not so marked as was that of alfalfa.

The correlation coefficient between aggregation and organic carbon, nitrogen, carbon-nitrogen ratio, or lime requirement was in every instance below the level of significance. Several investigators have emphasized the importance of organic matter in aggregate stability. The data herein presented suggest that, within limits of the experiment, the crop effect has greatly overshadowed organic matter as a factor in aggregate formation and stability. Retzer and Russell (18), Rogers (19), and Stauffer *et al.* (22) found no simple relationship between total carbon and degree of aggregation of field soils. Thus it appears that factors other than organic matter are largely responsible for aggregate formation under field conditions where different crops are grown.

Hide and Metzger (10) and Martin (12) have shown that the organic matter of well-aggregated material has a wider carbon-nitrogen ratio than does that of poorly aggregated material. On the other hand, Rost and Rowles (20) and Elson (9) could find no correlation between carbon-nitrogen ratio of the whole soil and aggregation. The results presented in table 1 suggested that any relationship that might exist between the carbon-nitrogen ratio of the whole organic matter of the soil and aggregation was nonsignificant in comparison to the differential influence of crops.

The apparent minor importance of calcium as a direct factor in the aggregation of soils has been observed by several investigators (4, 9, 14, 15, 16, 20). The results of this study merely add support to the general concept that lime is not so important in the aggregation of fairly normal field soils as was once assumed. Certainly the crop effect greatly overshadows any influence that the different calcium levels within the experimental plots may have had. If plant growth was sparse because of a deficiency of calcium, it appears probable that the addition of lime, which would increase the density of plant cover, would improve aggregation of the soil, not because the lime would have any direct influence on aggregation, but because of the improved crop growth and greater root development. Although the soils under investigation respond to lime, they will still produce, without liming, a reasonably good growth of most crops except alfalfa, sweet clover, and red clover.

Rogers (19) came to a different conclusion on the basis of his studies. From the photograph presented by him, however, it would appear that the difference in aggregation that he assigned to difference in calcium level may have been not the direct result of the calcium but rather its effect on the relative abundance of plant growth, which in turn altered the aggregation. His most acid plot is shown

to be almost free of vegetation, in contrast to an improved plant cover on the plots on both sides. Thus even Rogers' results do not seem to be out of line with the generalization that calcium will influence aggregation principally as a result of its influence on the relative abundance of biological activity within the soil.

Not only do the data from the experimental plots show a nonsignificant relationship between the calcium deficiency of the soil and the percentage of water-stable aggregates, but observations on the degree of soil crusting, across a wide belt of soils with various calcium contents, show essentially the same lack of relationship. In southeastern Kansas, as represented by this study, soils low in calcium are subject to severe crusting. This is not peculiar to soils with low levels of calcium saturation, however, as crusting of similar severity for a given rainfall intensity, crop, and surface condition occurs throughout the east-west belt of Kansas. On the western side of the belt the soil colloids are abundantly supplied with calcium. Also in this area free calcium carbonate occurs at the surface in some of the soils.

That aggregate formation and stability in prairie soils are probably highly biological is indicated by the effect of different crops as noted in this study and by the relationship of bacterial activity to aggregation in similar soils as noted by Myers and McCalla (15). Sufficient fertility elements are needed to enable the crop and other biological activities to bring aggregation to a high level. Because maximum aggregation is so highly biochemical it should be expected to be highly transitory. Substantiation of this idea was found in the results herein presented and in the study reported by Myers and McCalla (15). In both instances the high degree of aggregation due to the biological agent was reduced soon after the active agent was removed or reduced appreciably.

#### *Soils under grass of different ages or with different cover values*

The results of the study of the effect of grasses on soil aggregation and the relationship of aggregation to some soil factors are reported in table 3.

There was a marked difference in the aggregation of the soils under sods. The degree of aggregation showed a distinct relationship to the age of the sod. Also, the meadowland showed a somewhat greater degree of aggregation than did the overgrazed native pasture area. The correlation coefficients between aggregation and organic carbon and nitrogen were highly significant. This is indistinct contrast to the relationship shown in table 1. That aggregation was positively related to the content of soil organic matter where the crop was the same was evident. It was not evident from the data available whether the increased organic matter served directly by promoting aggregate formation or whether it served indirectly by protecting the soil from hydration due to the exceedingly low reversibility of dehydrated organic colloids after the aggregates were formed by other forces. Organic colloids through a physicochemical union with inorganic materials have been shown by Myers to increase aggregation directly after dehydration (14).

The physical effect of roots and the effect of organic matter on aggregation are difficult to separate because not only is organic carbon related to aggregation

where the type of crop is constant, but aggregation is also related to the length of time the crop is grown on a given area without cultivation. Organic accumulation in the soil is in turn directly related to the length of time the crop (grass) is grown undisturbed on the land. Furthermore, the annual root additions as organic matter (carbon and nitrogen) have accumulated in root channels formed as a result of root action. The biological activity associated with the roots (living and dead) could quickly produce aggregate cements (15) to bind the soil particles rearranged by the dynamic action of growing roots.

Likewise, where only grass as a cover was considered, the correlation coefficient between aggregation and the carbon-nitrogen ratio was significant. The degree of significance, however, was not of such great magnitude as in the case

TABLE 3

*Effect of age and condition of perennial plant cover (grass) on water-stable aggregates and some of the chemical properties of the soil*

AGE AND CONDITION OF COVER (GRASS)—1940	AGGREGATES COARSER THAN 0.105 MM. ( <i>N</i> = 18)	CHEMICAL NATURE OF SOILS ( <i>N</i> = 6)			
		Nitrogen	Organic carbon	Carbon Nitrogen ratio	Lime (CaCO <sub>3</sub> ) requirement
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>		<i>pounds</i>
Mixture of tame and native grasses 3 years old, cut annually, cover good....	57.8	0.122	1.58	13.0	3989
Mixed tame grasses, pastured moderately, cover good*.....	75.1	0.180	2.58	14.3	4000
Native virgin pasture, heavily grazed, cover fair.....	89.5	0.220	2.98	13.5	3979
Native virgin meadow, cover good.....	94.9	0.232	3.20	13.8	3915
Correlation coefficient ( <i>r</i> ) between aggregation and chemical factor of soil†....		0.980	0.967	0.555	—0.161

\* This area was in tame grass from 1928 to 1940 inclusive with the exception of the years 1933 and 1934 when it was planted to corn and oats, respectively.

† Value of *r* necessary for 5 per cent level of significance = 0.554; for 1 per cent level = 0.694.

of the relationship to organic carbon. Thus, it would appear that although the wide carbon-nitrogen ratio tended to be associated with an improved aggregation, where both the soil and the crop are fairly constant, it was not so important as the total amount of organic carbon in the soil.

The nonsignificance of the correlation coefficient between lime requirement and aggregation for soils growing the same type of crop suggested that, within the limits of the experiment, factors other than the lime content of the soil were more closely associated with aggregation and, therefore, possibly more important in bringing about changes in this condition. This would again suggest that the mineral nutrient level of the prairie soils is not of direct significance in aggregation but is of importance principally, if not entirely, through its influence on the biological and biochemical changes which bring about changes of great importance in aggregate formation and stability.



## SUMMARY

This study included the determination of degree of aggregation, the percentage of nitrogen and organic carbon, and the lime requirement of the soils of both cultivated and grass plots on two claypan soils of southeastern Kansas.

Differences in degree of aggregation, apparently due to the influence of the kind of crops grown, proved to be highly significant by statistical analysis.

An application of 8 tons per acre of manure had little effect on aggregation 6 months after application.

The use of manure, lime, and superphosphate as soil treatments and the growing of legumes in the rotation had no measurable carry-over effect on aggregation through succeeding periods of nonlegume cropping.

Where a tame grass mixture and alfalfa alone were grown undisturbed for 3 years, the alfalfa had the more favorable effect on aggregation.

Within the limits of this study, the possible effect of organic carbon, nitrogen, carbon-nitrogen ratio, or lime requirement on soil aggregation was overshadowed by the influence of different crops grown.

Results of this investigation support the contention that lime, as a direct factor in aggregation, is relatively unimportant.

On grass plots aggregation was positively associated with the organic carbon content of the soil. In the cultivated plots the differences due to crop far outweighed differences due to organic carbon, indicating the possibility that, under normal soil and crop conditions, factors other than organic carbon may be responsible for aggregate formation.

These results indicate that, although wider carbon-nitrogen ratio is associated with improved aggregation where the soil and crop are fairly constant, the relation of carbon to nitrogen is not so important as the total amount of organic carbon in the formation of soil aggregates.

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## BOOKS

*Distillers' Grain Manual.* By ROBERT T. WILKIE AND ROLLAND S. MATHER. Joseph E. Segram and Sons, Inc., Louisville, Kentucky, 1942. Pp. 56, illus. 11.

The origin, botany, and classification of corn, rye, barley, wheat, sorghum, and sugar cane are recorded in such detail as is required by those who are concerned with the distillery industry. Production records are shown for the more important producing states, and information is given on the handling of the grains from farms to the terminal markets and distilleries. The last chapter deals with grain by-products. Among other matters of considerable interest in the book are definitions for ergoty, garlicky, and weevily wheat and rye, and other grain standards.

*Regional Geography of Anglo-America.* By C. LANGDON WHITE AND EDWIN J. FOSDUE. Prentice-Hall, Inc., New York, 1943. Pp. 898, figs. 287. Price, \$4.75.

The reader of this book "will see how a people took possession of the land and how the land took possession of a people. He will become aware of the fact that the population is by no means evenly distributed through this living space, and that geographic factors are largely responsible for the uneven distribution." The book is of special importance to those who desire a better understanding of the influences which have fashioned the course of development of the country. Its illustrations are exceptionally well chosen and the manner of presentation of the material is such as to make most interesting reading. The discussion is based on the concept that "there are no new frontiers and that the future security of Anglo-Americans depends upon how well they use the land they already have."

THE EDITORS



# THE APPLICATION OF CONTROLLED DISPERSION TO THE TEXTURAL GRADING OF SOILS

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The preparation of soil samples for mechanical analysis and the subsequent classification into fractions according to size are carried out in different ways, depending on whether the investigation is concerned with agronomy, engineering, or pedology. The authors consider that in pedologic studies a preliminary treatment is necessary to break down the aggregates and liberate as completely as possible the particles smaller than  $2\mu$  in diameter; the classification will then give, as nearly as possible, the actual content of particles of the various sizes.

This criterion of mechanical analysis, which is essentially pedological, was advanced by Davis and Middleton at the First International Congress of Soil Science in 1927. On this basis, the soil is considered, not from the point of view of utility, but as a source of information. Analytical data thus obtained cannot be directly related to soil conditions in the field. They do, however, define a given soil property: the soil as constituted by individual particles classified according to size, that is, a well-defined *textural* property, which can be represented on pedological maps and which in research work can be related to other soil properties. Such a classification gives a close approximation of the content of particles less than  $2\mu$  in the soil, and forms a basis for the separation and characterization of the various soils. Actually, the dispersion methods used in mechanical analysis may also be used in the separation of the  $2\mu$  fraction; and the methods of control applied in the analysis, hereinafter described in detail, indicate whether the clay fraction has been isolated.

Once this purpose was clearly defined, the need became apparent for accurately established experimental techniques and for a controlled dispersion in order to determine to what degree the particles can be liberated from the aggregates and freed of their coatings (2).

In this paper two phases of mechanical analysis are considered: first, preparation of the sample, including dispersion, liberation, and cleaning of the particles; and second, direct and indirect controls of these operations.

## PREPARATION OF THE SAMPLES

According to the international method, air-dried material passing a 2-mm. screen is used for mechanical analysis. To eliminate the causes of aggregation, the sample is subjected to the following operations: dispersion of the soil colloid, oxidation of the organic matter, and breaking down of aggregates by gentle rubbing.

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*Dispersion of soil colloid*

The adsorbed ions are replaced by hydrogen ions as a result of shaking the soil sample with 0.1 per cent HCl for 5 minutes. In experiments with HCl of varying concentrations on calcium- and magnesium-loess pampeano (3), this concentration proved to be the minimum for efficient exchange. As exchange reactions soon reach equilibrium, a 5-minute period of contact was found to be sufficient. Table 1 shows that in this way 40 to 80 per cent of the adsorbed calcium and almost all the adsorbed magnesium are eliminated.

On contact for a second time with fresh 0.1 per cent HCl, the quantity of ions removed decreases appreciably. This is shown in table 2, which also indicates that three washings of the sample with 0.1 per cent HCl are practically enough to remove the bivalent ions originally present in the soil.

The use of the acid in such a low concentration brings about a very little loss in solution, which never amounts to 1 per cent. The greatest loss is shown by

TABLE 1

*Removal of calcium and magnesium ions from soil with 0.1 per cent HCl  
after 5 minutes' contact\**

Results in milliequivalents per 100 gm. oven-dry soil

SAMPLE NUMBER	ADSORBED $\text{Ca}^{++}$	$\text{Ca}^{++}$ REMOVED	ADSORBED $\text{Mg}^{++}$	$\text{Mg}^{++}$ REMOVED
449	11.4	6.30	2.3	2.10
795	2.5	1.10	1.9	0.35
796	4.0	2.20	1.5	0.60
837	14.8	8.30	3.6	3.00

\* Results for samples 370, 570, 716, 855, 919, and 753 are shown in table 2 under "1st washing."

samples high in organic matter. Table 3 shows the  $\text{SiO}_2$  and the  $\text{R}_2\text{O}_3$  loss of some samples.

After displacement of the adsorbed ions of the soil, the hydrogen ions are exchanged with Na ions, which give to the soil colloid a high stability. This replacement is effected by the use of 0.1 N NaOH, until the suspension attains a final pH value of about 9.

With this treatment, dispersion of the soil colloid is almost invariably good, but in some cases it is not sufficient, as for instance in samples from the lower horizons of soils developed on loess or loessial materials. In these cases, boiling the sample with 0.1 N (final concentration) NaOH in the presence of a few drops of 6 per cent hydrogen peroxide and gentle rubbing with the finger was successful. Table 4 shows the great differences in the fine-fraction content determined by the two methods.

In certain immature soils developed on sand dunes of the Post-pampeano in southern Santa Fe Province, complete dispersion of the fine material flocculated in a virtually irreversible form could not be obtained.

TABLE 2

*Removal of adsorbed calcium and magnesium through consecutive washings  
with 0.1 per cent HCl*

Results in milliequivalents per 100 gm. oven-dry soil

SAMPLE NUMBER	WASHING	Ca <sup>++</sup> REMOVED BY EACH WASHING	TOTAL Ca <sup>++</sup> REMOVED	TOTAL ADSORBED Ca <sup>++</sup>	Mg <sup>++</sup> REMOVED BY EACH WASHING	TOTAL Mg <sup>++</sup> REMOVED	TOTAL ADSORBED Mg <sup>++</sup>
370	1st	6.9	11.2	8.6	3.2	5.0	1.4
	2nd	3.1			1.2		
	3rd	1.2			0.6		
570	1st	10.07	17.57	12.8	1.9	3.3	1.7
	2nd	5.3			1.0		
	3rd	2.2			0.4		
716	1st	7.9	13.6	14.7	2.2	3.6	2.1
	2nd	4.1			1.0		
	3rd	1.6			0.4		
855	1st	6.4	13.9	15.7	2.9	5.1	1.9
	2nd	5.2			1.6		
	3rd	2.3			0.6		
919	1st	7.7	12.5	11.5	2.4	4.4	2.3
	2nd	3.3			1.3		
	3rd	1.5			0.7		
753	1st	6.1	10.4	10.4	4.0	6.0	2.5
	2nd	2.9			1.5		
	3rd	1.4			0.5		

TABLE 3

*Soil loss on solution by the acid treatment*  
Results in percentages of oven-dry soil

SAMPLE NUMBER	DISSOLVED SiO <sub>2</sub>	DISSOLVED R <sub>2</sub> O <sub>3</sub>
449	0.099	0.073
795	0.070	0.075
796	0.027	0.064
837	0.143	0.052
370	0.095	0.105
570	0.077	0.076
716	0.085	0.084
855	0.125	0.249
919	0.075	0.081
753	0.090	0.150
822	0.511	0.414
580	0.224	0.533
684	0.181	0.055
685	0.119	0.046



*Oxidation of organic matter*

Organic matter is found in appreciable quantities in only the A and B horizons of the soils of the Santa Fe Province, and even in these horizons it rarely exceeds 5 per cent. The degree of humification is variable; usually, however, the humified material is less than 50 per cent of the total organic matter content. Since it is this humified matter that must be destroyed in preparing the soil for mechanical analysis, an attempt was made to bring it into solution in order to make

TABLE 4

*Particles less than 2  $\mu$  in diameter in samples from lower horizons of soils developed on loess, as determined by the International dispersion method and by boiling with 0.1 N NaOH*

Results in percentages of oven-dry soil

SAMPLE NUMBER	HORIZON	PARTICLES LESS THAN 2 $\mu$	
		International dispersion method	Boiling with 0.1 N NaOH
595	BC	10.95	37.00
596	C	11.25	23.40
742	C	6.25	25.00
645	C	12.90	22.48
646	BCD	11.40	28.30
647	CD	6.20	21.30

TABLE 5

*Humus removal from soil by oxidizing treatment*

Results in percentages of oven-dry soil

SAMPLE NUMBER	ORGANIC MATTER	HUMUS	HUMUS LEFT AFTER TREATMENT
370	3.20	1.55	0.007
570	4.60	1.96	0.013
716	4.44	1.80	0.012
855	4.26	1.75	0.019
919	4.20	1.50	0.010
940	6.23	2.16	0.020
822	10.77	5.10	0.220
580	12.10	2.00	0.223
753	3.75	0.87	0.011

the attack easier and to allow use of an oxidizing agent of minimum concentration.

In the method adopted, all the humus is transformed into an alkaline water-soluble humate, which is then attacked. The sample is first boiled with water for half an hour, and the exchangeable bases are removed with 0.1 per cent HCl, as already explained. In making the reaction alkaline with 0.1 N NaOH, most of the humus goes into solution. It is separated by light centrifuging, treated with enough concentrated hydrogen peroxide to give a 2 per cent final concentration, and then boiled. The reaction is quick and complete, the end point

being shown by a definite change in color in all cases in which the humus content is high enough to interfere with the mechanical analysis.

If the humus is too high, the alkaline treatment is repeated. In this instance,  $\text{MnO}_2$ , which is very troublesome when hydrogen peroxide is used, does not interfere, as it is left in the sediment after centrifuging. Table 5 shows the extent to which humus is removed by this method.

#### *Disaggregation by gentle rubbing*

It was found very convenient to disaggregate the coarser fractions by gentle rubbing with the finger. This assures the resolving of the coarser aggregates into particles and aids in liberating them from their coatings. This action is particularly necessary for the red soils from Misiones and for those developed on loess, if the mechanical analysis is to serve the purpose outlined (4). That this treatment is effective is evident from the results obtained on two red soils dispersed according to the International method: the percentages of particles less than  $2\mu$  in sample 65 were 72 with rubbing and only 46.35 without rubbing, and the corresponding percentages in sample 69 were 68.8 and 35.64.

#### *Recommended technique of dispersion*

On the basis of the results shown, the following technique of soil dispersion for mechanical analysis is recommended: 50 gm. of air-dried soil is boiled with 200 cc. of distilled water for half an hour. After cooling, enough  $\text{HCl}$  is added to bring the total volume to 0.1 per cent concentration. The acidified sample is shaken for 5 minutes, centrifuged, and the liquid decanted off. This acid treatment is applied three times.<sup>3</sup>

The operation is followed by application of the qualitative test for calcium to a small portion of the clear liquid. When necessary, a fourth washing is made, at the same concentration.

The sample next is shaken with 100 cc. of distilled water, centrifuged, and the liquid decanted off. To the residue, 200 cc. of distilled water is added and the mixture shaken. The suspension is brought to a pH value of about 10 with  $\text{NaOH}$  and shaken for 15 minutes. Then the degree of alkalinity is adjusted, and the suspension is lightly centrifuged. The darker suspension containing the greater part of the humus as alkaline humate and some clay<sup>4</sup> is poured off. To the liquid is added 10 cc. of Perhidrol (hydrogen peroxide, 130 volumes concentration). This is then slowly brought to boiling and concentrated to one third of the original volume. If there is no definite color change, another 10 cc. of Perhidrol is added, the volume made up to 200 cc., and boiled again.

The color change shows the success of the operation. To the coarser fraction remaining from the centrifuging, 200 cc. of 6 per cent hydrogen peroxide is added, and the treatment is repeated. If but little humus is present, Perhidrol of lower concentration may be used, as for example 2 per cent.

<sup>3</sup> When  $\text{CaCO}_3$  is present in the soil, enough  $\text{HCl}$  is added to destroy it completely. This is followed by shaking, centrifuging, and then the acid treatment as directed.

<sup>4</sup> In samples high in humus a second alkaline treatment is necessary.

After this oxidizing treatment, the sample generally becomes flocculated. Both portions are reunited and centrifuged, and the liquid is decanted off. About 200 cc. of distilled water is added to the residue, and the suspension is made alkaline with NaOH, to a pH value of about 10, and shaken for 10 minutes.

#### CONTROL OF OPERATIONS

The dispersion of the sample should bring about the most complete liberation of the particles, with the greatest possible dispersion of the soil colloids and the most effective cleansing from surface coatings. As it cannot be claimed that a given technique attains this objective *in every case*, it is necessary to determine the degree of success and thus to enable evaluation of the significance of the results of subsequent classification according to size. As a control, observations are made during the analysis; these may be followed by the use of some simple relationships which show whether the analysis has met the requirements of the pedological criterion (2). The methods are classified as *direct* and *indirect*, according to whether they are applied during mechanical analysis or whether subsequent tests or determinations are required.

Of the direct methods, only two are presented in this paper: that of the petrographic microscope and that of the logarithmic graph.

#### *Direct methods*

*Petrographic microscopy.* Microscopic observation of the fractions obtained in the mechanical analysis serves as a test not only of the degree of separation of the aggregates into their individual particles, but also of the elimination of the surface coatings of the particles. Observations are made with transmitted or reflected light: by the use of polarized light further differentiation between aggregates and clean, cemented or crystalline particles is possible. Two series of observations are made: those on material greater than  $53\mu$  in diameter, and those on material less than  $53\mu$ .

Among the forms observed were the following, which led to special investigations on the nature of the cements and coatings found, in order to determine the most adequate treatment:

Colloid-coated crystals found in a red soil (Misiones) after application of the International-A dispersion method (fig. 1).

Round forms remaining after application of the International-A dispersion method. Actually these are aggregates of cemented crystalline particles. They disaggregate when rubbed with the finger.

Aggregates resistant to the International-A dispersion method but which are broken down by boiling with 0.1 N NaOH and rubbing with the finger. Aggregates shown in figure 2 are from a typical loess.

Volcanic glass containing ducts filled with cement or fine particles, resistant to the International-A dispersion method. Such material can be cleaned by boiling with 0.1 N NaOH and rubbing with the finger (fig. 3).

Crystals with a very rough surface, which cannot be cleaned by the alkali and rubbing methods. The crystals shown in figure 4 are from a soil developed on sand dunes.

Volcanic glass coated with cement. Figure 5 shows some of the fragments that were resistant to the International-A dispersion method. After boiling with 0.1 N NaOH and rubbing with the finger, the appearance is very different, as shown in figure 6.



FIG. 1



FIG. 2

FIG. 1. COLLOID-COATED CRYSTALS FOUND IN A RED SOIL (MISSIONES) AFTER APPLICATION OF THE INTERNATIONAL-A DISPERSION METHOD

FIG. 2. TYPICAL LOESS SOIL AGGREGATES, RESISTANT TO THE INTERNATIONAL-A DISPERSION METHOD

They can be broken down by boiling with 0.1 N NaOH and rubbing with the finger



FIG. 3



FIG. 4



FIG. 5

FIG. 3. FRAGMENTS OF VOLCANIC GLASS CONTAINING DUCTS FILLED WITH CEMENT OR FINE PARTICLES RESISTANT TO THE INTERNATIONAL-A DISPERSION METHOD

They can be cleaned by boiling with 0.1 N NaOH and rubbing with the finger

FIG. 4. ROUGH CRYSTALS FROM A SOIL DEVELOPED ON SAND DUNES

They are resistant to cleaning by the alkali and rubbing methods

FIG. 5 VOLCANIC GLASS COATED WITH CEMENT AND RESISTANT TO THE INTERNATIONAL-A DISPERSION METHOD



FIG. 6



FIG. 7

FIG. 6. CRYSTALS SIMILAR TO THOSE IN FIGURE 5 AFTER BOILING WITH 0.1 N NaOH AND RUBBING WITH THE FINGER

FIG. 7. AGGREGATES OF FINE PARTICLES RESISTANT TO THE INTERNATIONAL-A DISPERSION METHOD

Aggregates of fine particles resistant to the International-A dispersion method. These are very small crystals cemented into an opaque mass (fig. 7), which on boiling with 0.1 *N* NaOH and rubbing, generally resolves into fine particles.

*The logarithmic graph.* The results of the mechanical analysis (1) are expressed in the usual graphic form, the logarithm of the maximum diameter of the granules being plotted on the abscissa and the corresponding accumulated percentage on the ordinate. If instead of the percentage we plot its logarithm, a more illustrative graph within the range of 1 to 20 $\mu$  is obtained. This method of plotting was suggested by James in 1934 (7).

For many of our soils it was found that between these limits the logarithmic graph is a straight line, provided that the grading of the soil is regular, that the dispersion of the soil colloid is good, and that coagulation does not occur during the

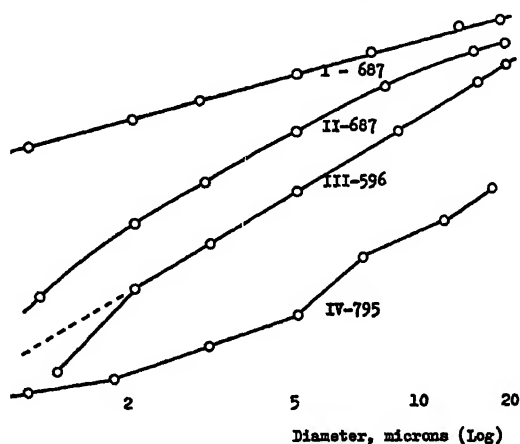


FIG. 8. LOGARITHMIC GRAPHS AS TESTS OF THE ACCURACY OF THE MECHANICAL ANALYSIS OF SOILS

I, Regular grading; sedimentation without coagulation. II, Dispersion failure. III, Possible coagulation. IV, Predomination of one fraction (67.7 per cent, 20–200 $\mu$ ).

*sedimentation process* (curve I, fig. 8). In this case, between the percentage of particles  $P$  and the corresponding maximum size  $D$  the following relation holds:

$$\log P = m \log D + K$$

in which slope  $m$  and the constant  $K$  are characteristic of the soil.

In applying this method to our soils, it was found further that when one size-fraction predominates, the curve is not a straight line (curve IV); when the dispersion method is not adequate, the curve drops more rapidly (curve II); and when coagulation occurs, the last readings are faulty, and therefore the last points fall below the line (curve III).

This graphic presentation has all the advantages of a straight line plotting, such as easy construction and easy and reliable interpolation. It gives a simple criterion which can be used as a guide for controlling the dispersion, which is of

immediate application, and which necessitates no other test or determination subsequent to mechanical analysis.

### *Indirect methods*

Among the relationships used as an indirect control of the results of mechanical analysis, the most noteworthy is that between the base-exchange capacity ( $T$  value) of the original sample and its clay and humus contents.

As a first approximation, it is supposed that this relation is of the type

$$T = \alpha A + \beta H \quad (1)$$

where  $A$  is the percentage of fraction smaller than  $2\mu$ ,  $H$  the humus content, and  $\alpha$  and  $\beta$  the exchange capacities in milliequivalents per gram of clay and of humus respectively.

In an investigation on soil samples containing humus formed under very different natural conditions, an approximately constant adsorption coefficient of 5.5 m.e. per gram was found (5). Equation (1) can therefore be written in the form

$$\alpha = \frac{T - 5.5H}{A} \quad (2)$$

The coefficient  $\alpha$  has been the subject of special research (6):—From typical soils 22 selected samples were separated into two fractions, one including all the particles greater than  $2\mu$ , and the other, particles smaller than  $2\mu$ . The technique used in the preparation of the sample was that described for mechanical analysis, and the separation was controlled with the petrographic microscope. The base-exchange capacity of each fraction was determined, with the following results:

The base-exchange capacity of the fraction smaller than  $2\mu$  varied between the limits  $0.45 \leq \alpha \leq 0.67$ , in milliequivalents per gram of fraction.

The clean samples of the fraction greater than  $2\mu$  had almost no base-exchange capacity.

The base-exchange capacity of the entire fraction greater than  $2\mu$  varied between 0 and 0.054 m. e. per gram, the higher values corresponding to samples for which the microscope showed the occurrence of aggregates and coatings.

In applying formula (2), therefore, a value for  $\alpha$  must be obtained within the given range, otherwise the results of the analysis may be doubtful.

### SUMMARY

This paper points out that the mechanical analysis of soil, from a pedological point of view, should show the soil composition in mineral particles after these have been freed as completely as possible of cements and surface coatings. The content of particles less than  $2\mu$  in diameter can be determined most accurately. Experimental conditions that must be met in the adequate preparation of soil samples for mechanical analysis are described in detail. Results of investigations on soil colloid dispersion and oxidation of organic matter, as well as the

experimental technique developed from these investigations, are given. Direct and indirect control methods are described for determining the degree of separation and cleansing of the particles, and for evaluating the results obtained.

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# SOME ACIDIC PROPERTIES OF ALKALI LIGNIN<sup>1</sup>

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Soil organic matter has been shown to consist principally of lignin or a lignin-humic complex (10, 12). Among other roles, this material serves as an absorbent of free ions and as an agent in transferring ions from minerals to the soil colloids and eventually to the plant (1, 6, 7). Are these properties due to functional groups in lignin or are they dependent upon alterations of the lignin molecule which occur in the soil?

This paper is a report on experiments conducted on purified alkali lignin, in order to determine the possible role of lignin in the absorption of minerals by plants. Since this process concerns principally the exchange capacity of lignin, the emphasis is placed upon the quantitative and qualitative aspects of the acidic groups. The former aspect deals with the magnitude of the exchange capacity and some of the factors which affect it; the latter deals with an evaluation of the strength of the acids involved.

## MATERIALS AND METHODS

### *Corncob lignin*

Finely ground corncoobs were extracted in a Soxhlet extractor with a solution of alcohol-benzene for 8 hours. The extracted material was dried, then extracted exhaustively with a solution of cold 4 per cent sodium hydroxide. The filtered extracts were neutralized and then acidified with sulfuric acid to make a 3 per cent acid solution. The contents were then refluxed at the boiling point for 4 hours to hydrolyze the hemicelluloses. The residue, crude lignin, was washed free of acid, dried, powdered, and further purified with alcohol and acetone. Lignin prepared in this manner is called "alkali lignin." It contained 0.06 per cent ash and 0.7 per cent nitrogen. This fraction was used in all the following experiments.

### *Base exchange*

Determinations of base exchange were made by titrating the electro dialyzed sample electrometrically with 0.1 *N* potassium hydroxide to a pH of 7. The number of milliequivalents of potassium required for 100 gm. of material was then calculated. The base was added in quantities of 1 to 2 ml. per 24 hours and allowed to stand with frequent stirring.

### *Mobilization tests*

In order to test the ability of isolated lignin to mobilize ions from minerals, the following procedure was used. Crystals of calcite weighing about 3 gm.

<sup>1</sup> Contribution No. 469 of the Massachusetts Agricultural Experiment Station.



were smoothed on the corners to avoid mechanical losses, treated with acid, then carefully washed, dried, and weighed. Such crystals, in triplicate, were placed in perforated test tubes (25 by 200 mm.), which were inserted in cork stoppers of sufficient size to fit wide-mouthed bottles containing the suspension of electro-dialyzed lignin. Each bottle was equipped with a stirrer by which the suspension could be agitated. By weighing the crystals at intervals and by the use of control tests, losses in the weight of the crystals due to the mobilization of ions by lignin could be determined.

Electrodialysis was brought about in a Mattson cell, using 110 volts for approximately 150 hours.

A glass electrode was used in all electrometric work.

#### THE QUANTITATIVE ASPECT OF THE ACIDIC GROUPS OF LIGNIN

In making base-exchange determinations on lignin in an aqueous suspension, the granular appearance of the material indicated that a maximum reaction might not be taking place. Lignin when precipitated by acids from an alkaline solution consists of fine and apparently fully hydrated particles of a gel-like appearance. In order to approach this condition as nearly as possible the precipitated lignin was kept in such a state during its preparation for tests. In this condition the exchange value was approximately 122 m.e. per 100 gm. of lignin in contrast to 15 m.e. obtained on the air-dried material.

To determine further the variations in exchange values, aliquots of the same suspension were brought to dryness on a steam bath at about 85°C. This treatment lowered the enhanced values to approximately 11 m.e. Subsequent treatment of this material in the manner described above increased this value to almost that of the original. In general, these results indicate that changes in exchange values observed on drying are due chiefly to an inactivation of the base-binding groups. It seems more fitting, therefore, to speak of the potential exchange capacity of isolated lignins, since this phenomenon appears to be largely dormant in dried samples. It is known that colloidal humus behaves like a highly hydrated suspensoid; hence, perhaps it is not unreasonable to suspect that hydration plays a considerable part in the behavior of organic matter even at this stage. The loss of base-exchange capacity upon drying may be due in part to dehydration.

McGeorge (10, 11) noted that leaching of lignin and lignohumates with basic hydroxides, hydrochloric acid, and a solution of a salt such as an acetate, which will yield hydroxyl ions on hydrolysis, increased the exchange capacity. He believed that this change was probably due to hydrolysis. Lein (9) believed that sodium hydroxide oxidized certain substances, thereby increasing the exchange capacity. Increases obtained by Lein, however, were considerably smaller than those recorded by McGeorge or those indicated in this paper.

In the belief that increases in base-exchange values of soil organic matter may be due in part to progressive oxidations, samples were subjected to alkaline oxidation (5). This procedure indicated an oxidation value of 172 ml. of 0.1 *N* iodine per gram of lignin. One of the products formed was iodoform. This

has been<sup>7</sup> obtained by similar treatment of lignin from other sources (8, 13). This product could be produced by the action of sodium hypoiodite upon some of the proposed 3-carbon compounds that are believed to be attached to the aromatic nucleus of lignin. The oxidized lignin appeared to be considerably more highly peptized than the usual preparations. Base-exchange determinations on the electrolyzed material indicated an increase of about 35 per cent. The increase is due probably to the presence of the carboxyl group.

† Mobilization tests on electrolyzed lignin over a period of about 6 months indicated an ability to remove calcium from crystals of calcite. The extent

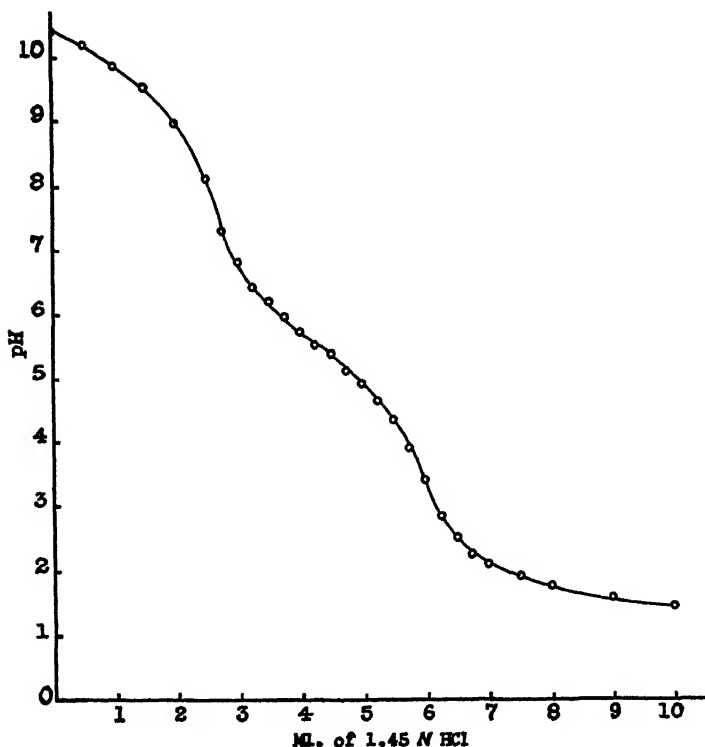


FIG. 1. TITRATION CURVE OF PURIFIED ALKALI LIGNIN FROM CORNCOALS

of the transfer was equivalent to an exchange value of about 150 m.e. per 100 gm. of lignin. The reaction is slow and continues over a long period.

#### THE QUALITATIVE ASPECT OF THE ACIDIC GROUPS OF LIGNIN

In order to determine the qualitative factor of acidic groups of lignin, investigators have titrated some fraction of humus electrometrically with a base. The curves derived from these titrations, with few exceptions (3, 4), have shown only slight breaks and hence reveal very little information.

Contrary to the usual practice, isolated lignin was dissolved in a dilute solution of a strong base and subsequently titrated electrometrically with a rel-

atively concentrated solution of a strong acid. Preliminary trials indicated that the best results were obtained by saturating a solution of 0.065 *N* potassium hydroxide at 25 C. with electrodyalized lignin for  $\frac{1}{2}$  hour, filtering off the excess, and titrating the filtrate with 1.45 *N* hydrochloric acid. The results obtained are plotted in figure 1.

The middle section of the curve, indicating buffer action, is attributed directly to the lignin complex. It is realized that the conditions for the occurrence of the reaction are not ideal, yet in more dilute solutions the same characteristics in the curve are noted, but the intensity is not so great. At this zone, buffer action should be great, since the effective system is composed of weak acids and their potassium salts. The weak acids would buffer against bases; and their potassium salts, against acids. The region of greatest buffer action is from about pH 4.5 to pH 6.5. It is worthy of note that the buffering power comes at a pH which is within the range of the reaction of a great many soils.

In order to gain at least an approximation of the strength of the acids involved, use was made of the equation  $\text{pH} = \text{PK}_a + \log \frac{[\text{salt}]}{[\text{acid}]}$ . From this formula (2) it follows that the greatest buffering power against either acid or base occurs when the ratio of the components of the last member is 1-1, or when the hydrogen-ion concentration is equal to the ionization constant of the acid; or at the point of half neutralization. Such a point is located at approximately pH 5.5. Thus the  $\text{PK}_a$  for the acid is equal to 5.5 which is equivalent to an "apparent ionization constant" of about  $3.16 \times 10^{-6}$ .

#### SUMMARY AND CONCLUSIONS

Experiments were conducted on purified alkali lignin in order to determine the role of lignin in the absorption of minerals by plants.

It was noted that the exchange capacity of isolated lignin may be inactivated by drying at low temperatures and that it can be reactivated to a considerable extent by dissolving in a basic solution and purifying in the hydrated state.

Oxidation of lignin resulted in an increased exchange capacity.

When a suspension of electrodyalized lignin was placed in contact with crystals of calcite, a loss of calcium was noted equivalent to an exchange capacity of about 150 m.e. per 100 gm. of lignin.

A titration curve obtained by treating, with hydrochloric acid, lignin dissolved in potassium hydroxide indicates that considerable buffer action from salts occurs over the range pH 4.5-6.5 and that the apparent ionization constants of acids which might contribute are of the order  $3.16 \times 10^{-6}$ .

The foregoing observations would indicate the following: (a) The exchange capacity of isolated alkali lignin may be partly dependent upon hydration, and it may be increased by oxidation; (b) electrodyalized lignin exerts a mobilizing effect upon minerals; (c) acids having an "apparent ionization constant" of the order  $3.16 \times 10^{-6}$  may be present, in which case their salts exert a buffer effect greatest between pH 4.5 and 6.5. In general, it may be said that purified alkali lignin has many of the properties characteristic of soil organic matter.

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# RELATIONSHIPS OF NATURAL VEGETATION TO THE WATER-HOLDING CAPACITY OF THE SOILS OF NEW ENGLAND<sup>1</sup>

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With the growth of plant ecology, the more definite physical and chemical properties of the soil were associated with plant distribution within a given region. Naturally there has been much disagreement among those actively engaged in the study of plant and soil relationships, probably because soil and climatic conditions vary tremendously the world over. In fact, such differences of opinion led to the establishment of two schools of thought. The chemical nature of the soil was cited by one school as having the greatest significance in natural distribution of plants, whereas the other school contended that the physical properties of the soil exerted the most influence upon the presence or absence of particular plant species or associations within a given locality. Of the different chemical and physical properties of the soil considered in this connection, perhaps the hydrogen-ion concentration and the moisture relations of the soil have been studied the most intensively. These factors have been credited as exerting much influence upon plant cover, although results indicate that relationships existing in one region do not necessarily occur in other localities that have been under observation.

Today, the concensus among those interested in the subject seems to be that both the hydrogen-ion concentration and the moisture relations of the soil, among other factors, play important roles in governing the type of vegetation growing within a given region, much depending upon particular situations under question.

## REVIEW OF LITERATURE

In a survey of the vegetation on Oak Island, near Boston, Massachusetts, made in 1902, Rich (12) reported 400 different species growing but discussed no relationships between soil and flora.

Hilgard (8) wrote extensively on the recognition of character of soils from their native vegetation and presented many data to show that certain plant species grow on soils of a particular chemical and physical make-up. He was especially interested, however, in chemical factors of the soil as influencing vegetation. He stressed the point that an ecological analysis aids materially in making a general estimate of the agricultural value of land.

Fernald (3) studied soil preferences of certain alpine and subalpine plants occurring in New York, New England, and eastern Canada. He concluded that "... the alpine plants are much more dependent upon the chemical constituents of the soil than has been generally supposed."

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Tillotsun (13) asserted that the physical properties of the soil, particularly the available soil moisture, are of the utmost importance in regard to the differences in plant growth and plant formations.

Brooks (1), in 1914, offered suggestions for judging the value and adaptation of land in New England. The soils were classified as inferior, good, the best, on the basis of depth and color of surface soil, depth of water table, soil texture, nature of subsoil, and natural vegetation. For each of the three types of soils, certain herbs, shrubs, and trees were found to be characteristic. It was suggested that, in general, the physical properties of the soil, especially the water-holding capacity, are most influential in controlling distribution of flora, though it was asserted that some plant species do best on soils of a particular soil reaction.

In an intensive study of soil and plant relationships in Tooele Valley, Utah, Kearney *et al.* (9) made various laboratory tests on soil samples collected in areas of different flora. The results showed great differences in the physical and chemical properties of the soils. Consequently, the conclusion was reached that a certain plant or plant association in that region indicated a soil of certain moisture and salinity properties, all of which could be used in estimating value of land for various agricultural purposes.

From a detailed study of the Pine Barrens in New Jersey, Harshberger (5) concluded that soils with a low moisture-holding capacity supported the growth of certain plants, whereas other soils with a comparatively higher moisture-holding capacity were characterized by the presence of still other species.

Results of an extensive ecological survey by Pearson (11) in the San Francisco Mountain region of Arizona seemed to indicate that chemical properties of soil were not the limiting factors in controlling the distribution of plants within a region of uniform climatic conditions. On the other hand, his work indicated that certain physical properties of soil; namely, water-holding capacity, wilting coefficient, and permeability, were of great consequence in respect to plant distribution.

Craib (2) has done a considerable amount of research work in New Hampshire on aspects of soil moisture in the forest and its relation to vegetation. Of special interest was the idea that the index of productivity of a soil can be measured by the maximum volume and the actual volume of available water the soil holds.

Hicock *et al.* (7), working in Connecticut, attempted to establish relationships between forest composition and certain soil characters. Their results indicated that in the particular region studied there was apparently no real correlation between vegetation and specific soil types. When the soils were classified into four broad groups on a basis of moisture conditions, however, some relationship did exist between these groups and the vegetation. The lack of correlation between certain plants and specific soil types was explained as follows: first, that certain soil types might be biologically equivalent, and secondly, "the climatic conditions within the region in which the studies were made are generally favorable to the development of fairly luxuriant plant growth. The ecological margin of safety in the region is rather wide and it is reasonable to suppose that the general excellence of climatic factors may compensate to some extent for poverty of certain soil conditions."

Lawrence<sup>3</sup> conducted a land cover survey in Washington County, Rhode Island, for the purpose of correlating major vegetation units with soil series. His results showed a correlation between flora and soil. Such edaphic factors as soil moisture, relative fertility, and physical state of soil were considered extremely important in regard to soil and plant relationships. Several plant species were cited as being characteristic of particular soil series. No correlation seemed to exist between vegetation and soil type, or between brush and soil series. The point was stressed that certain soil types may be biological equivalents.

<sup>3</sup> Lawrence, G. H. M. A study of the influence of soil upon vegetation: A correlation between major vegetation units and soil series in Washington County, Rhode Island. 1933. [Unpublished thesis, R. I. State College, Kingston.]

Further, the idea was set forth that "there is a high degree of correlation between productivity of soil series as evidenced by natural vegetation growing upon them, and the degree of selection on the basis of productivity—made by the agriculturist in the growing of cultivated crops."

As a result of research work in the Lake States region, Wilde (16) reported the following features to be of prime importance in correlating soils with forest growth: underground water, topography, soil texture, soil structure, and nature of soil profile. Water was considered to be a very important factor governing distribution of species, since soils constantly influenced by a high water table (peats, mucks) and poorly drained soils were usually characterized by the presence of certain definite plant species. Soils not influenced by the water table supported a forest stand determined by the texture of the soil. For each of the various textures of these soils, characteristic associated plant species were listed, though it was explained that such a classification might lead to difficulties, since other factors must be considered.

Turner (14) reported that certain soil-topographic features are extremely important in influencing the distribution of forest types in Arkansas. Important factors considered were degree of slope and its effect on drainage, depth of soil, and physical structure of horizons. Several different soils, varying in these factors, were examined, and for each, certain forest types were listed as characteristic. The importance of soil water and plant relationships was stressed.

#### PURPOSE OF THE INVESTIGATIONS

The influence of soil conditions on the natural distribution of plants has been studied fairly intensively in scattered regions of this country and elsewhere, but it has received comparatively little attention in New England. If certain plant and soil relationships could be uncovered, therefore, they might add to existing knowledge on the subject, and any information obtained might be valuable as a basis for future work in this area.

The purpose of the study, therefore, was to establish relationships between the maximum water-holding capacity of certain soils in New England and the vegetation growing on these soils. The maximum water-holding capacity was chosen as a typical physical property for investigation, since any factor that affects soil moisture to an appreciable degree is important in relation to the growth of plants. Inasmuch as the B horizon, as well as the A horizon, has an important effect on the growth of plants, both were considered in this investigation. Furthermore, the purpose of the study was, not to discuss reasons for the occurrence of particular plants on different soils, but merely to present a picture of the situation as it was found in the field.

#### EXPERIMENTAL PROCEDURE

Field work was conducted during the year 1938 at stations in widely scattered sections of New England. Areas under direct observation were selected carefully in order that vegetation studied should be as nearly typical of the locality as possible. All sites were selected on land not now or recently under cultivation. During the course of the field work, 30 different soil series were encountered, thus ensuring a wide variety of soil conditions.

A special form was devised for recording field data, including the number and the location of the station, the date, the soil type, the various plant species and



the number of each growing within a designated area, and other ecological notes. Space was also provided for computing the maximum water-holding capacity and recording the pH of both the A and B horizon soil samples taken at each station.

A modification of the "belt transect" system (15) was employed in listing the species and number of trees and shrubs growing on a definite area of soil. A 50-foot steel tape was used as a transect line, and the species and numbers of individuals occurring within 3 feet of this line were recorded. In several instances, more than one transect line was established, especially in regions that exhibited a wide variety of species. Naturally, such a system must be used with much discrimination in order to make fair comparisons between the various stations examined.

The transect lines established for surveying the trees and shrubs were used as a basis for studying the herbaceous cover. List quadrats, 1 yard square, as described by Weaver and Clements (15) were located along the transect lines, a yardstick and pegs being used to establish the quadrats accurately. This type of quadrat seemed most applicable in this case, for as Hanson *et al.* (4) have said, "... the purpose of the quadrat and the nature of the vegetation are major factors in determining method to employ." Here again, the species and numbers of each were recorded, the average number of individuals for each species per quadrat being reported for the station.

During the survey, over 200 species were recorded, though for many of these, insufficient information was obtained to warrant statistical analysis. Throughout the entire study the common names of the plants concerned have been used; Latin names for these appear in the glossary.

The only trees considered were those having a minimum height of  $4\frac{1}{2}$  feet. Also, because of habit of growth, certain plants did not lend themselves to statistical analysis. Hence, low blueberry, huckleberry, and Kentucky bluegrass were reported on an estimated percentage of ground cover. Furthermore, figures presented for broomsedge are on the transect basis, whereas wintergreen was tabulated on the quadrat basis.

Soil samples of both the A horizon and the B horizon were taken at each station. To ensure a fair sample, several borings were made with a soil auger ( $1\frac{1}{2}$  inches in diameter) along each transect line, and a composite sample from these borings was made. Samples were kept in standard soil boxes until needed for further use.

The water-holding capacities of the A and B horizons were determined in the laboratory according to the Hilgard method as outlined by Lyon, Fippin, and Buckman (10) with a few minor changes. Instead of starting with a definite weight of air-dried soil, wetting the soil, and then weighing it again, the samples were first wetted, then weighed, dried for 24 hours at  $110^{\circ}\text{C}$ ., and weighed a second time. The percentage of water retained was calculated on a dry soil basis. It is realized that such capacities obtained cannot be considered as actual values normally occurring in undisturbed soil but rather as comparative values.

## PRESENTATION AND DISCUSSION OF DATA

*Maximum water-holding capacity of the soil and plant distribution*

For convenience in tabulating data, the water-holding capacities, which varied from approximately 30 to 130 per cent for various soils collected, were grouped into 10 classes, each covering an interval of 10 per cent. According to this purely arbitrary system, the number of stations represented in each class is shown in table 1 for both the A and the B horizon samples. As would be expected, the numbers of stations represented by the two horizons in corresponding classes differ, since the moisture-retaining power of the topsoil and of the sub-surface soil at a given station differs, the subsurface almost always holding less water than does the surface layer.

Since an equal number of stations was not represented in each water-holding capacity class, as indicated in table 1, it was necessary to resort to comparative

TABLE 1

*Number of stations represented in each water-holding capacity class of soil considered*

CLASS	HORIZON A	HORIZON B
30-40	22	42
40-50	22	33
50-60	32	44
60-70	27	28
70-80	28	19
80-90	23	16
90-100	15	7
100-110	7	0
110-120	6	0
120-130	7	0

figures in order to reveal any true relationships that might exist between plant species and water-retaining power of soil. Hence, each plant species was treated separately in the following manner:

1. The number of individuals occurring in each water-holding class was determined from data on field sheets.
2. The average number of individuals per quadrat or per transect, as the case might be, was found for each class of soils by dividing the total number of plants obtained for each capacity class (step 1) by the number of stations represented in that particular class.
3. The average numbers of individuals per station for the various classes (step 2) were added to obtain the sum total of the average number of individuals per station.
4. Finally, the relative abundance in per cent for each water-holding capacity class was computed by dividing the various values obtained in step 2 by the sum found in step 3 and multiplying the result by 100.

Accordingly, table 2 shows relative abundance, in per cent, of certain plants present in each soil water-holding capacity class recognized.

In order to study the picture more clearly, a purely arbitrary system, based

TABLE 2

*Relative abundance of certain plants in each water-holding capacity class of soil considered*

PLANT	SOIL HORI- ZON	ABUNDANCE OF PLANTS IN WATER-HOLDING CAPACITY CLASSES OF SOIL										MEAN WATER- HOLDING CAPACITY OF SOIL
		30- 40	40- 50	50- 60	60- 70	70- 80	80- 90	90- 100	100- 110	110- 120	120- 130	
		per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	
Alder (speckled)	A				18	47	15	12			8	81.1 $\pm$ 1.56
	B		8	13	29	42	8					67.9 $\pm$ 1.05
Anemone	A			9	8	14	18	20			31	93.7 $\pm$ 2.38
	B			23	20	36	21					70.5 $\pm$ 1.06
Arrow-wood	A		1	2	1	3	14	35	26		18	99.4 $\pm$ 1.61
	B	8	18	1	19	16	19	12	7			70.7 $\pm$ 2.06
Ash (white)	A			10	8	6	10	21	32		13	88.3 $\pm$ 1.63
	B		1	16	21	35	20	7				72.8 $\pm$ 1.17
Beech	A			1	4	10	9	9	39		28	102.80 $\pm$ 1.82
	B		1	10	15	60	14					78 $\pm$ 1.11
Bellwort	A				1	8	7	13	19	11	41	108.8 $\pm$ 1.70
	B					30	12	58				87.8 $\pm$ .90
Birch (black)	A	5	9	4	23	21	16		17	5		75.9 $\pm$ 2.12
	B	9	16	23	11	37	4					61.3 $\pm$ 1.44
Birch (canoe)	A	4	2	2	8	8	6	13	34		23	96.5 $\pm$ 2.40
	B	5	9	11	18	20	37					70 $\pm$ 1.53
Birch (gray)	A	9	26	18	18	10	5		13		1	63.10 $\pm$ 2.18
	B	20	23	18	13	9	10	7				57.6 $\pm$ 1.86
Birch (yellow)	A		4	3		32	61					79.30 $\pm$ .95
	B	10	7	83								52.3 $\pm$ .63
Blueberry (low)	A	7	1	18	50	14		5			5	66.80 $\pm$ 1.79
	B	14	27	17	2	40						57.7 $\pm$ 1.54
Blueberry (high)	A		5	4	7	11	14	21	26	7	5	90.7 $\pm$ 1.98
	B	1	11	10	7	38	28	5				72.4 $\pm$ 1.42
Broomsedge	A	18	48	22	11	1						47.9 $\pm$ .92
	B	65	26	9								39.4 $\pm$ .65
Buttercup	A			7	4	16	21	4	36		12	92.9 $\pm$ 1.93
	B		10	7	45	18	2	18				69.9 $\pm$ 1.45
Cherry (choke)	A	36	12	17	8	13	5	7	2			55.30 $\pm$ 2.06
	B	16	29	17	13	11	7	7				57.3 $\pm$ 1.78

TABLE 2—Continued

PLANT	SOIL HORI- ZON	ABUNDANCE OF PLANTS IN WATER-HOLDING CAPACITY CLASSES OF SOIL										MEAN WATER- HOLDING CAPACITY OF SOIL
		30- 40	40- 50	50- 60	60- 70	70- 80	80- 90	90- 100	100- 110	110- 120	120- 130	
		per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	
Cinnamon fern	A			2		21	7	17	18	17	18	99.9 $\pm$ 1.86
	B		55	9		18		18				60.30 $\pm$ 1.97
Cinquefoil	A	15	5	28	30	6	9	4	3			61.5 $\pm$ 1.72
	B	21	9	46	24							52.3 $\pm$ 1.05
Dandelion	A					10	17		50		23	103.2 $\pm$ 1.57
	B		11		43	22		24				72.2 $\pm$ 1.51
Elm (American)	A			1	1	7	20	13	24		34	103.50 $\pm$ 1.82
	B		23	8	17	18	34					68.2 $\pm$ 1.56
False lily of the valley	A	2	1	1	5	5	13	6	1	12	54	107.8 $\pm$ 2.37
	B	3	2	10	3	38		44				81.40 $\pm$ 1.51
Flowering dog- wood	A				23	62	15					74.2 $\pm$ .61
	B			38	43	10	9					64 $\pm$ .91
Hardhack	A		2	5	6	23	9	8	22	10	15	93.4 $\pm$ 2.19
	B	1	16	22	31	8	18	4				64.9 $\pm$ 1.45
Hemlock	A	1	1	17	14	10	8	34	6		9	83.4 $\pm$ 2.14
	B	3	37	20	16	4	6	14				60.5 $\pm$ 1.81
Hickory	A	2		3	15	11	26	32	5	6		85 $\pm$ 1.59
	B		1	15	42	33	9					68.4 $\pm$ .87
Huckleberry	A		29	15	6	46	4					63.1 $\pm$ 1.38
	B	33	24	4	18	21						52.0 $\pm$ 1.58
Indigo	A	70	22			8						40.4 $\pm$ 1.1
	B	57	23				20					47.30 $\pm$ 1.93
Ironwood	A			5	2	5	14	34	31		9	95.8 $\pm$ 1.56
	B			27	47	7	19					66.8 $\pm$ 1.03
Jack-in-the pulpit	A				4	1	25	25			45	104.6 $\pm$ 1.94
	B		55	4			41					61.8 $\pm$ 1.94
Kentucky blue grass	A			2	2	4	17		23		52	109 $\pm$ 1.94
	B		3	1	24	12	16	44				81.9 $\pm$ .41
Lady's slipper	A	12	28	1	7	30		7	4	11		67.90 $\pm$ 2.54
	B	9	17	24		17	26	7				65.5 $\pm$ 1.89
Lespedeza	A	30	48	12	10							45.2 $\pm$ .91
	B	87	9	4								36.7 $\pm$ .47

TABLE 2—Continued

PLANT	SOIL HORI- ZON	ABUNDANCE OF PLANTS IN WATER-HOLDING CAPACITY CLASSES OF SOIL										MEAN WATER- HOLDING CAPACITY OF SOIL
		30- 40	40- 50	50- 60	60- 70	70- 80	80- 90	90- 100	100- 110	110- 120	120- 130	
		per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
Lupine	A	67	33									38.3 ± .47
	B	95	5									35.5 ± .22
Maple (red)	A	3	6	5	16	8	9	14	14	12	13	88.6 ± 2.57
	B	1	10	25	8	20	14	22				71.60 ± 1.75
Maple (sugar)	A	2	1	2	9	10	13	17	32		14	93.9 ± 2.05
	B	1	10	16	19	22	25	7				70.40 ± 1.49
Meadow-sweet	A		1	1	6	21	6	14	23	10	18	97.2 ± 2.01
	B		6	12	20	19	35	8				73.9 ± 1.37
Mountain laurel	A	6	3	25	22	16	21	7				68.00 ± 1.56
	B		17	60	11	8	4					57.20 ± .95
Mouse-ear chick- weed	A					2	20	10	52		16	102.60 ± 1.29
	B			8	35	40	17					71.60 ± .85
Oak (black)	A	55	6	12	11	11	5					48.2 ± 1.67
	B	42	40	9		9						44.4 ± 1.15
Oak (red)	A	3	7	6	11	10	13	19	29		2	84.2 ± 2.15
	B	4	6	16	21	18	18	17				71.5 ± 1.66
Oak (scarlet)	A		16	6	18	26	9	6	6	7	6	76.9 ± 2.31
	B	3	15	12	6	34	26	5				70.1 ± 1.60
Oak (scrub)	A	60	23	6	9			2				42.4 ± 1.21
	B	80	14	5	1							37.7 ± .60
Oak (white)	A	2	10	14	23	12	11	8	11	9		75.7 ± 2.21
	B	6	19	11	19	11	9	25				68.7 ± 2.00
Pitch pine	A	55	29	11	4			1				41.9 ± .99
	B	74	13	11	1			1				39.4 ± .91
Plantain (com- mon)	A					12	11	5	31		41	106.9 ± 1.78
	B			3	23	20	20	34				80.9 ± 1.25
Plantain (English)	A						13	25	44		18	103.5 ± 1.21
	B				16	35	24	25				80.8 ± 1.03
Red cedar	A	2	25	15	9	35	10	4				64.6 ± 1.56
	B	8	57	29	6							48.30 ± .71
Sarsaparilla	A	8	3		17	28	9	1	1	2	31	86.9 ± 2.93
	B	5	22	15	17	41						61.7 ± 1.34

TABLE 2—*Concluded*

PLANT	SOIL HORIZON	ABUNDANCE OF PLANTS IN WATER-HOLDING CAPACITY CLASSES OF SOIL										MEAN WATER-HOLDING CAPACITY OF SOIL
		30-40	40-50	50-60	60-70	70-80	80-90	90-100	100-110	110-120	120-130	
		per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
Sensitive fern	A					70	3	13			14	84.9 $\pm$ 1.75
	B		58	9	33							52.5 $\pm$ .92
Shad bush	A		18	7	18	20	3	10		13	11	79.4 $\pm$ 2.68
	B	39	3	3	3	45	7					58.3 $\pm$ 1.99
Sheep laurel	A			2	9	24	22	28	8	6	2	87 $\pm$ 1.47
	B		1	32	40	17	10					65.3 $\pm$ .96
Shrubby cinquefoil	A					4	16	1	16	19	44	111.2 $\pm$ 1.61
	B		5		19	5	25	46				83.3 $\pm$ 1.43
Skunk cabbage	A					10	32	38			20	88.6 $\pm$ .82
	B		34	8	4		54					68.2 $\pm$ 1.87
Sorrel	A	3	13	18	35	2	15	11	3			67.4 $\pm$ 1.73
	B	9	4	29	47	11						59.7 $\pm$ 1.04
Spotted winter-green	A	3	28	2	21	7	13	26				69.4 $\pm$ 2.04
	B	8	6	18	14	21	33					68.3 $\pm$ 1.60
Spruce (Canadian)	A				14	6	16	19	37	3	5	93.8 $\pm$ 1.61
	B			1	2	64	20	13				79.3 $\pm$ .78
Strawberry	A	7		4	2	7	12	5	34	14	15	96.7 $\pm$ 2.44
	B	7	6	6	29	16	12	24				72.3 $\pm$ 1.79
Sweet fern	A	3	40	30	21	3	2	1				54.10 $\pm$ 1.09
	B	41	15	41	3							45.6 $\pm$ .97
Violet (bird-foot)	A		40	53	7							51.70 $\pm$ .60
	B	92	8									35 $\pm$ .27
White pine	A	7	7	14	7	9	10	14	13	4	15	83.4 $\pm$ 2.81
	B	8	19	14	13	7	14	25				68.4 $\pm$ 2.09
Wild oat grass	A	4	16	29	50	1						57.8 $\pm$ .88
	B	23	29	17		18	13					55 $\pm$ 1.76
Wintergreen	A		5	18	20	20	5	27			5	76.3 $\pm$ 1.93
	B		14	32	20	13	21					64.50 $\pm$ 1.36
Witch-hazel	A		11	5	24	8	15	16			21	83.5 $\pm$ 2.42
	B	4		12	25	33	26					71.1 $\pm$ 1.22

on values obtained in this investigation, has been devised dividing the water-holding capacity range into three major groupings as follows:

30-60 per cent represents comparatively low water-holding capacity.

60-90 per cent represents medium water-holding capacity.

90-130 per cent represents a comparatively high water-holding capacity.

*Plants characteristic of soil having a comparatively low water-holding capacity*

Several species of plants seem to be characteristic of the lighter soils of New England. Some plants usually found growing on well-drained areas, where both the topsoil and the subsoil hold little water, are pitch pine, black oak, sweet fern, scrub oak, broomsedge, lespedeza, indigo, bird-foot violet, lupine, and cinquefoil. In general, these plants were most abundant on the following soil series: Carver, Chicopee, Hinckley, Merrimac, and Plymouth, all of which (with the exception of Plymouth) are outwash soils, light in texture, and underlain by stratified sand and gravel. Wilde (16) reported the occurrence of black oak and shrub oak on the poorer sandy soils of the Lake States region and the abundance of sweet fern on the moraine sands. Pitch pine and scrub oak were listed by Lawrence<sup>3</sup> as being common on the well-drained, sandy soils of southern Rhode Island. Hicock *et al.* (7) have recorded the abundance of black oak on certain lighter well-drained soils of Connecticut. In the pine barren region of New Jersey, Harshberger (5) found that pitch pine and scrub oak grew abundantly on soils having a maximum water-holding of about 45 per cent and that black oak was indigenous to soil holding about 56 per cent moisture. Hazard (6) observed in New Hampshire that near broomsedge and low blueberries were found an occasional white pine, pitch pine, gray birch, cherry, and red maple. Brooks (1) pointed out that the poorer soils of Massachusetts supported the growth of such plants as broomsedge, lespedeza, rabbit-foot clover, lupines, gray birch, scrub oak, scarlet oak, and pitch pine.

Figure 1 shows the relative abundance, as found in this study, of three species typical of soil having a low water-holding capacity.

*Species characteristic of soil in which horizon A has a medium water-holding capacity and horizon B a comparatively low capacity*

On soils in which the water-holding capacity of horizon A is medium and that of horizon B is comparatively low, low blueberry, huckleberry, mountain laurel, and wild oat grass were present in the greatest numbers. Low blueberries were noted by Wilde (16) as growing the most abundantly on sandy soils. Harshberger (5) and Hazard (6) were of similar opinion.

*Plants characteristic of soil having a medium water-holding capacity*

Black birch, flowering dogwood, hickory, sheep laurel, white oak, scarlet oak, and wood sorrel have been noted growing on a wide variety of soils, but generally these plants were most abundant in areas where both the topsoil and the sub-surface soil were found to have a medium water-holding capacity. Wilde (16) found white oak, red oak, and canoe birch to be common on the better sandy

soils. Red maple, flowering dogwood, white oak, and pitch pine were cited by Harshberger (5) as being common on the deciduous forest soils.

The aforementioned species cannot be considered as a group commonly occurring on certain soil series, because many other ecological factors must be taken into consideration, several of which are not as yet fully understood.

The relative abundance curves for black birch and sheep laurel determined in this study are given in figure 2.

*Species most abundant on soil having a comparatively high water-holding capacity*

A fairly large number of plants were found in greatest abundance in soils in which the water-holding capacity of the A horizon was relatively high and that of the B horizon medium. These include the following species: anemone, ash, beech, bellwort, high blueberry, buttercup, dandelion, ironwood, Kentucky blue-

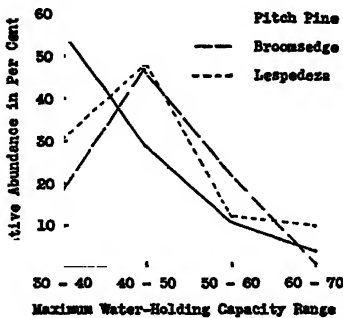


FIG. 1

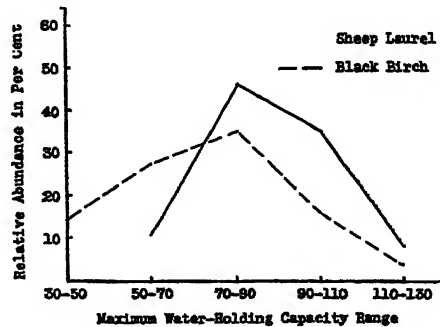


FIG. 2

FIG. 1. PLANTS FREQUENTLY FOUND GROWING IN SOIL OF LOW WATER-HOLDING CAPACITY

FIG. 2. PLANTS FREQUENTLY FOUND GROWING IN SOIL OF MEDIUM WATER-HOLDING CAPACITY

grass, sugar maple, meadow-sweet, mouse-ear chickweed, red oak, common plantain, English plantain, shrubby cinquefoil, spruce, and wild strawberry.

Brooks (1) observed that sugar maple, white oak, and black oak were indicators of the "good soils" in New England, and that elm, beech, ash, and Kentucky bluegrass were typical of the "best" New England soils. His classification was of a very general nature, to be sure, but many of the results obtained in this investigation seem to support several of his conclusions, although much rests upon how his soil classification is interpreted. Hazard (6), in her investigation, noted that beech, ash, sugar maple, spruce, white oak, and red oak were associated with the better forest soils.

Figure 3 pictures the relative abundance of three species which, in this study, were found growing in the greatest quantities on soils having comparatively high moisture-retaining capacities.

*Plants apparently indifferent to the water-holding capacity of the soil*

A considerable number of species studied were found growing on soils varying widely in their moisture-retaining properties. Gray birch, choke cherry, false



lily of the valley, hemlock, lady's slipper, red maple, red cedar, sarsaparilla, shad bush, spotted wintergreen, white pine, wintergreen, and witch-hazel were among those of widespread occurrence. Table 2 reveals that several of these plants, gray birch and choke cherry, for example, are more abundant in one soil class than in another, but in general their range of tolerance is not narrow in respect to the water-holding capacity of the soil.

Both Wilde (16) and Hazard (6) have demonstrated that white pine occurs on a wide variety of soils. Red maple, wild black cherry, and false lily of the valley were classified by Hicock *et al.* (7) as being well represented on all types of soil although red maple was most common on the poorly drained and organic soils. Lawrence<sup>3</sup> found that no definite relationship exists between distribution of gray birch and soils on which the plant exists.

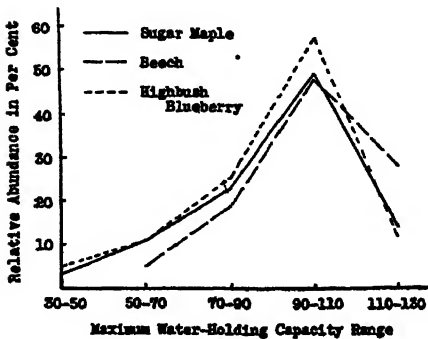


FIG. 3



FIG. 4

FIG. 3. PLANTS FREQUENTLY FOUND GROWING IN SOIL OF HIGH WATER-HOLDING CAPACITY  
FIG. 4. PLANTS FOUND GROWING IN SOILS OF BOTH LOW AND HIGH WATER-HOLDING CAPACITIES

Figure 4 presents curves for three plants that were found, in this investigation, to be common on several soil types.

#### *Plant distribution and biologically equivalent soil types*

Several plants, notably arrow-wood, elm, hardhack, skunk cabbage, sensitive fern, hemlock, red maple, cinnamon fern, and yellow birch, were often found on soils in which the maximum water-holding capacity of the topsoil varied widely from that of the subsurface soil. Although the subsurface soil held much less water than the topsoil, the water table was invariably high. Thus these plants, usually characteristic of moist soil conditions, may or may not indicate the moisture-holding capacity of the soil. Hence, despite the comparatively low water-holding capacity of the sandy subsurface layers of such soil series as Whitman and Scarboro, plants such as those named occur on these soils, since we have a biologically equivalent soil condition as explained by Hicock *et al.* (7) in respect to plant distribution. In other words, the high water table or poor drainage compensates for the inability of the subsurface soil to hold water. Wilde also found such plants as alder, ash, elm, red maple, yellow birch, willow, and white

pine growing in abundance on soils under permanent or partial influence of the water table.

## SUMMARY

The maximum water-holding capacity of the solum has been found to be a factor in the natural distribution of some plants. Exception must be made, however, in the case of soils that are under the direct influence of the water table, as previously explained by Wilde (16) and others. Results of a study in widely scattered sections of New England indicate that certain trees, shrubs, and herbs grow in the greatest abundance on soils of particular water-holding ranges, whereas other species are indifferent to this soil factor as influencing their natural distribution.

The natural vegetation of an area may serve as an indication of the value of soil incident to growing a crop without increased risk of drought or pressure of excessive moisture.

## GLOSSARY

Alder (speckled).....	<i>Alnus incana</i> (L.) Moench.	Elm (American).....	<i>Ulmus americana</i> L.
Anemone.....	<i>Anemone quinquefolia</i> L.	False lily of the valley.....	<i>Maianthemum canadense</i> Desf.
Arrow-wood.....	<i>Viburnum dentatum</i> L.	Flowering dogwood..	<i>Cornus florida</i> L.
Ash (white).....	<i>Frazinus americana</i> L.	Hardhack.....	<i>Spiraea tomentosa</i> L.
Beech.....	<i>Fagus grandifolia</i> Ehrh.	Hemlock.....	<i>Tsuga canadensis</i> (L.) Carr.
Bellwort.....	<i>Uvularia perfoliata</i> L.	Hickory.....	<i>Carya</i> spp.
Birch (black).....	<i>Betula lenta</i> L.	Huckleberry.....	<i>Gaylussacia baccata</i> (Wang.) C. Koch.
Birch (canoe).....	<i>Betula alba</i> var. <i>papyrifera</i> (Marsh.) Spach.	Indigo.....	<i>Baptisia tinctoria</i> (L.) R. Br.
Birch (gray).....	<i>Betula populifolia</i> Marsh.	Ironwood.....	<i>Carpinus caroliniana</i> Walt.
Birch (yellow).....	<i>Betula utea</i> Michx.	Jack-in-the-pulpit....	<i>Arisaema triphyllum</i> (L.) Schott.
Blueberry (low).....	<i>Vaccinium pennsylvanicum</i> Lam.	Kentucky bluegrass..	<i>Poa pratensis</i>
Blueberry (high).....	<i>Vaccinium</i> spp.	Lady's slipper.....	<i>Cypripedium arietinum</i>
Broomsedge.....	<i>Andropogon scoparius</i> Mishx.	Lespedeza.....	<i>Lespedeza capitata</i>
Buttercup.....	<i>Ranunculus bulbosus</i> L.	Lupine.....	<i>Lupinus perennis</i>
Cherry (choke).....	<i>Prunus virginiana</i> L.	Maple (red).....	<i>Acer rubrum</i>
Cherry (wild black)..	<i>Prunus serotina</i>	Maple (sugar).....	<i>Acer saccharum</i>
Cinnamon fern.....	<i>Osmunda cinnamomea</i> L.	Meadow-sweet.....	<i>Spiraea latifolia</i>
Cinquefoil.....	<i>Potentilla canadensis</i> L.	Mountain laurel....	<i>Kalmia latifolia</i>
Dandelion.....	<i>Taraxacum officinale</i> Weber.	Mouse-ear chickweed.	<i>Cerastium vulgatum</i> L.
		Oak (black).....	<i>Quercus velutina</i> Sam.
		Oak (red).....	<i>Quercus rubra</i> L.
		Oak (scarlet).....	<i>Quercus coccinea</i> Muench.

Oak (scrub).....	<i>Quercus ilicifolia</i> Wang.	Skunk cabbage.....	<i>Symplocarpus foetidus</i> (L.) Nutt.
Oak (white).....	<i>Quercus alba</i> L.	Sorrel.....	<i>Rumex acetosella</i> L.
Pitch pine.....	<i>Pinus rigida</i> Mill.	Spotted wintergreen.	<i>Chimaphila umbellata</i> (L.) Nutt.
Plantain (common)...	<i>Plantago major</i> L.	Spruce.....	<i>Picea canadensis</i> L.
Plantain (English)...	<i>Plantago lanceolata</i> L.	Strawberry.....	<i>Fragaria virginiana</i> Duchesne.
Red cedar.....	<i>Juniperas virginiana</i> L.	Sweet fern.....	<i>Myrica asplenifolia</i> L.
Sarsaparilla.....	<i>Aralia nudicaulis</i> L.	Violet (bird-foot)....	<i>Viola pedata</i> L.
Sensitive fern.....	<i>Onoclea sensibilis</i> L.	White pine.....	<i>Pinus strobus</i> L.
Shad bush.....	<i>Amelanchier canadensis</i> (L.) Medie.	Wild oat grass.....	<i>Danthonia spicata</i> (L.)
Sheep laurel.....	<i>Kalmia angustifolia</i> L.	Wintergreen.....	<i>Gaultheria procumbens</i> L.
Shrubby cinquefoil...	<i>Potentilla fruticosa</i> L.	Witch-hazel.....	<i>Hamamelis virginiana</i> L.

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# MAGNESIUM DEPLETION IN RELATION TO SOME CROPPING SYSTEMS AND SOIL TREATMENTS<sup>1</sup>

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The concept that plant nutrition is an exchange process between adsorbed ions on the colloidal fraction of the soil and the hydrogen ions on the roots (3, 4) naturally directs attention to the cations on the list of the plant nutrients. Among these, calcium and its singular activities have already had fruitful consideration (1, 2, 5). Studies have revealed the more or less baffling behavior of potassium that still is challenging attempts at explanation (7). Magnesium has been the subject of little research (9) in the glacial soils, though it has had attention in soils more highly developed (8). Consideration may well be given to the magnesium supply and its exchange activities between the soil complex and the plant as these are related to the continued and sufficient delivery of this nutrient for utilization by the plant.

Now that calcium is becoming a common soil treatment, its companion cation, magnesium, deserves attention. This is particularly timely if we are to learn of its behavior in connection with the heavy lime applications given many soils. Then, too, the declining soil fertility manifested in greater magnesium-deficiency symptoms in plants, particularly the soybeans, must naturally demand early attention to magnesium in the soil. Because of these facts, magnesium was given exploratory attention in two soil studies. One consisted of a survey of the magnesium supplies in the soil as revealed by rapid tests in 600 soil samples collected in the State of Missouri during 2 years. Another study involved analytical attention to the soils of some of the plots from the research station at Bethany, Missouri, in cooperation with the Soil Conservation Service. In these, particular attention was given to certain cropping systems and soil treatments as they are related to the depletion of magnesium.

## MAGNESIUM IN MISSOURI SOILS

Of numerous samples received by the laboratory for tests, those which could be specifically classified as to soil type were used. In addition, samplings were made specifically for this study. Though about 100 soil types of Missouri were represented, the bulk of the samples were from approximately 12 of the most common types.

The tests of magnesium were made according to the rapid method of Bayer

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and Bruner (6). The soil was leached with 0.3 *N* hydrochloric acid, and the magnesium was precipitated as a colloidal hydroxide colored with titian yellow. The values used by Bayer and Bruner as standards ranged from 0.25 to 2.00 m.e. magnesium per 100 gm. of soil or from 60 to 480 pounds per acre 2 million. The medium figure was taken as 240 pounds per acre. Soils containing less were

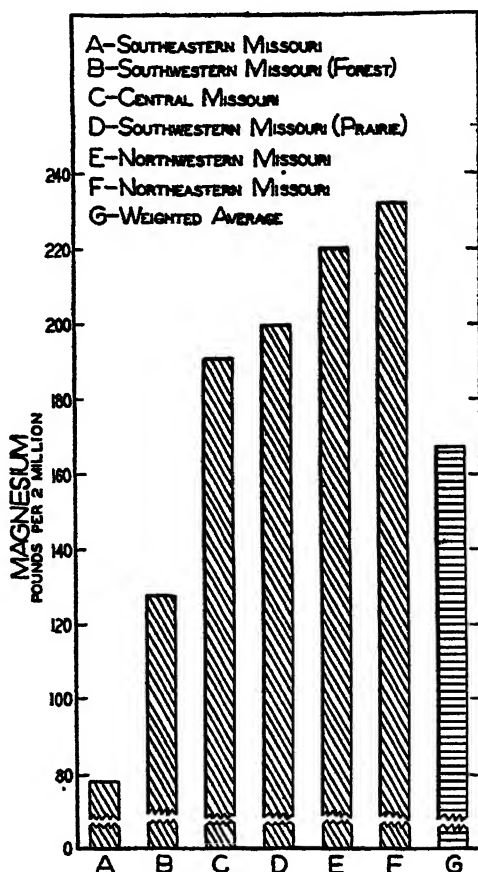


FIG. 1. EXCHANGEABLE MAGNESIUM, AS POUNDS PER ACRE, IN THE SOILS IN DIFFERENT AREAS OF MISSOURI

adjudged as "low" and those containing more were considered "high" in magnesium.

The results of this inventory are presented graphically in figure 1, which shows the soils as groups in the different geographic areas of the state. Two of the areas, namely, the southeastern part and the southwestern prairie were not represented by a sufficient number of samples. They are included, nevertheless, for their indicative values. The samples of the former of these two areas are all sandy loams. The remainder of the soils for the state were mainly silt loams.

The less leached soils contained the more magnesium. Those progressively

more developed showed lower contents of this plant nutrient. The most significant revelation of this inventory is the fact that even the area of soils with the highest magnesium content did not reveal as much as 240 pounds per acre, considered as medium in amount. The mean for the 600 samples of the state was 168 pounds per 2 million. Thus, either all the soils of Missouri are significantly low in magnesium, in general, or the standards set for this test by Bayer and Bruner (6) are too high.

That the soils of Missouri may be generally low in magnesium is suggested by numerous cases of plant symptoms indicating magnesium deficiencies, particularly on soils with crops in close sequence under reduced amounts of plowing. Further suggestion comes from studies by Graham (10). When he used the separated silt fraction from an Iowa surface soil after it had been treated with acid clay, the magnesium content of the crop grown on it was no higher than that

TABLE 1

*Changes in degrees of saturation of the soil complex by calcium and magnesium and in the organic matter and nitrogen contents of the soil from 1931 to 1937*

CROP AND SOIL TREATMENT*	SATURATION BY		PERCENTAGE OF	
	Calcium	Magnesium	Organic matter	Nitrogen
Bluegrass—no treatment.....	Increase	Decrease?†	Increase	Increase
Alfalfa—lime plus phosphate‡.....	Increase	Decrease	Increase	Increase
Rotation—lime plus phosphate.....	Increase	Decrease	Increase	Increase?
Rotation—no treatment.....	Decrease	Decrease?	Decrease	Decrease
Fallow surface—no treatment.....	Decrease	Increase	Decrease	Decrease
Fallow subsoil—no treatment.....	Decrease	Increase	Decrease	Decrease

\* Complete data were reported by Whitt and Swanson (13, table 3) for these treatments and crops.

† Where the data are not entirely consistent in their trend for all of the four determinations, 1931, 1933, 1935, 1937, the general trend is given with a question mark.

‡ Phosphate and lime were applied in 1930, and phosphate at three-year intervals thereafter.

of the planted seed. These observations suggest that there may be insufficient exchangeable magnesium on the colloidal fraction of the soil, and insufficient active reserve of this element in the silt portion of even the recently glaciated soils. Such facts suggest attention to possible magnesium shortages for crops on Missouri soils of older glaciations and of more intensive development at higher temperatures.

#### CROPPING SYSTEMS, SOIL TREATMENTS, AND POSSIBLE MAGNESIUM DEPLETION

In connection with the research work at the Soil Conservation Experiment Station on Shelby loam, a glacial drift soil, the exchangeable calcium and magnesium were determined in differently treated soils sampled to surface depths at three biennial intervals representing a total of 7 years (1931–1937) in the history of the treatments (13). Similar determinations were made at the end of the fourth biennial period on successive 1-inch soil layers down to 13 inches

in the permanent bluegrass sod in the plot series. Determinations were made, at the same time, of the nitrogen and of the organic matter by means of carbon. The soils sampled and studied for magnesium, included (a) three plots in a rotation of corn, wheat, clover-timothy, with no treatment, (b) similar plots with lime plus phosphate, (c) alfalfa with lime plus phosphate, (d) bluegrass with no treatment, (e) fallow treatment on a surface soil, and (f) similar treatment on an exposed subsoil. It was on only the permanent bluegrass sod that the samples were taken as 1-inch layers in 1939. The other samples were taken as the surface 7 inches in a single sampling, several samplings being composited in each case for the plot.

The changes in the amounts of exchangeable calcium and magnesium with time in these soils under different treatments direct particular attention to the magnesium. These trends along with those for the percentages of carbon and of nitrogen during the 7 years represented by four successive analyses are listed in table 1.

#### *Decrease in magnesium saturation under apparent soil improvement*

It is particularly noteworthy that though the shifts in calcium saturation, in organic matter, and in nitrogen were generally in the same direction, the shifts in magnesium saturation seemed to be in the opposite direction. Under those crops and soil treatments which have commonly been considered as soil-building, e.g., the use of lime and phosphate, the growing of alfalfa and bluegrass, or those that demonstrate trends toward increase in the organic matter, in the nitrogen, and in the degree of calcium saturation in the soil, there was a trend toward decrease in the degree of magnesium saturation of the soil. This was true for crops that allowed a minimum of erosion to bring soil from the lower into the upper layers through plowing. Then again, the rotation and the fallowing—all without soil treatment—which give a decrease in the organic matter, in the nitrogen, and in the calcium saturation, serve to give an increase in magnesium saturation. Here higher magnesium saturation in the subsoil layer plowed into the surface as a consequence of truncating the profile by erosion may be responsible. Thus, while soils were improving in calcium saturation and in nitrogen and organic matter content under little or no erosion, the magnesium saturation was decreasing. Contrariwise, while soil depletion with respect to calcium saturation, nitrogen, and organic matter was occurring along with possibly some erosion, the degree of magnesium saturation was increasing in this soil.

This suggests that the lower crop production and the fallowing, which allow exchangeable calcium to be lowered in concentration while some erosion is occurring, serve to increase the degree of saturation of magnesium. Bluegrass, however, without soil treatment has entirely the opposite effects. Its effects on the soil correspond with what happens when either a legume-containing rotation or continuous alfalfa is given lime and phosphate. Bluegrass is thus a soil-builder as shown by comparison of these soil properties.

That the bluegrass crop, without soil treatment, is singular in this respect among these limited numbers of cropping systems tested is further supported by

the quantitative data from the 1-inch layers of the soil in the grass sod. This is indicated by the distinct differences between the upper seven 1-inch layers of surface soil and the lower six layers of subsurface soil. This was a profile that was not being truncated by erosion and was not given lime and phosphate, yet the surface soil bearing the bluegrass roots was decidedly low in magnesium saturation in contrast to the subsurface. The data are assembled in table 2.

TABLE 2

*Degree of soil saturation by calcium and magnesium, and percentages of organic matter and nitrogen in the surface and subsurface layers of permanent bluegrass\**

BLUEGRASS	SATURATION BY				PERCENTAGE OF		C/N
	Calcium		Magnesium		Organic matter	Nitrogen	
	<i>per cent</i>	<i>m.e.</i>	<i>per cent</i>	<i>m.e.</i>			
Surface seven 1-inch layers, mean.....	61.3	11.74	19.4	3.30	3.73	0.180	11.98
Subsurface six 1-inch layers, mean.....	56.9	15.52	30.4	8.28	2.06	0.106	11.22
Difference due to bluegrass roots.....	4.4		11.0		1.67	0.074	0.76
	Increase		Decrease		Increase	Increase	Increase

\* This plot was seeded to bluegrass with timothy in 1930. It had been in cultivated crops previously. Complete data for the successive 1-inch layers were reported by Whitt and Swanson (13, table 2).

TABLE 3

*Increasing organic matter, nitrogen, and calcium saturation and decreasing magnesium saturation in a treated soil growing alfalfa\**

DATES OF SAMPLING†	EXCHANGE CAPACITY	SATURATION BY				PERCENTAGE OF	
		Calcium		Magnesium		Organic matter	Nitrogen
	<i>m.e.</i>	<i>per cent</i>	<i>m.e.</i>	<i>per cent</i>	<i>m.e.</i>		
1931	18.95	58.10	11.01	21.16	4.01	3.79	.184
1933	19.17	64.79	12.42	17.06	3.27	3.91	.186
1935	20.02	87.71	17.56	17.33	3.47	4.05	.196
1937	19.72	77.33	15.25	16.84	3.32	4.02	.192

\* These data were reported by Whitt and Swanson (13, table 3).

† Soil treated in 1930.

Here again the soil zone bearing the many bluegrass roots and experiencing the effects of the crop was higher than the subsurface with its few roots, in those respects that represented increase with time (table 1); namely, organic matter, nitrogen, and calcium saturation, whereas it was much lower in magnesium saturation than the subsurface. Bluegrass apparently built up the soil in some respects while it was depleting the active magnesium supply in the absence of erosion.



Alfalfa as a crop with the soil treatments of limestone and phosphate was similar to bluegrass under no treatment in giving increases in the organic matter, the nitrogen, and the degree of calcium saturation, while the degree of magnesium saturation was decreasing. This is shown by the data in table 3.

*Increase in calcium saturation and decrease in magnesium saturation  
after liming*

Where the limestone was applied for alfalfa in 1930, as shown in table 3, the calcium saturation, and with it the organic matter and nitrogen, mounted steadily until 1935. By 1937 the calcium saturation was declining, though it was still almost 20 per cent above the value given by the determination in 1931. By that late date the contents of organic matter and of nitrogen were no higher than those of the sampling immediately previous. While these three factors were increasing, the degree of magnesium saturation was decreasing. According to these data, the alfalfa crop on the soil given lime and phosphate was reducing magnesium saturation more drastically than was the bluegrass on the same soil without treatment. The reduction was even more drastic under alfalfa than under rotation on the soil given limestone and phosphate. These reductions in magnesium under alfalfa were coincidental with an increase in the saturation of the soil by calcium.

Bluegrass without limestone applications was bringing about an increase in calcium saturation of the soil colloid similar to that under limed alfalfa. This movement of limestone, for 5 years, from the applied crystalline into the adsorbed form on the soil colloid and the resultant increasing saturation may be the explanation of the better legume crop growth with time after limestone applications. The increased calcium saturation under bluegrass without lime applications has been suggested by Whitt (12) as an explanation for the periodic advent of white clover in bluegrass sods.

While the soils under cropping with no erosion (alfalfa and bluegrass) were undergoing reduction in magnesium saturation and increase in calcium saturation, those under fallow, with erosion, were showing the opposite effects. The cases under study were not numerous enough to warrant generalizations; nevertheless, they suggest that soil-conserving crops and soil treatments are associated with lowered magnesium saturation and that erosive crops are associated with increased magnesium saturation. Though the degree of magnesium saturation was reduced by bluegrass without soil treatment, it was reduced more by rotation with lime and phosphate treatments, and still more by alfalfa with these same soil treatments. Whereas bluegrass raised the percentage of calcium saturation by one fourth, it lowered the magnesium saturation by one twentieth. For the rotation with lime and phosphate, the saturation went upward as much as one third for the calcium and downward one fifth for the magnesium. Under fallow and erosion, the surface soil decreased in calcium saturation equivalent to about one twentieth but increased in magnesium saturation as much as one seventh. The desurfaced soil, or exposed subsoil, under fallow decreased in calcium saturation by about one twelfth but increased in magnesium as much as one third during the 6 years.

*Truncation of profile in relation to changes in magnesium saturation*

Truncation of the profile by erosion on the 8 per cent slope may offer an explanation of the increase in magnesium saturation in the fallow soils. What truncation was doing was shown by the successive 1-inch layers (13) which were studied only under the bluegrass sod where no erosion took place. If we assume that the bluegrass crop was without disturbing effects at depths of 7 to 13 inches, and that the profiles of the bluegrass and of the fallow surface plots were the same at the outset, then if truncation from 1930 to 1937 were to increase the magnesium saturation of the fallow surface plot to the figure of 23.37 per cent as a mean of the upper seven 1-inch layers, this would represent a shift downward in the profile to approach the mean magnesium figure of 22.63 per cent under bluegrass for the seven 1-inch layers ranging from the depths 3 to 9 inches inclusive, or the mean figure 24.57 per cent for the depths from 4 to 10 inches inclusive. This would demand truncation by erosion to the extent of 3 to 4 inches in 7 years, or the surface 7 inches in 14 years. Coincidentally, the erosion data for these 7 years (13) showed that this plot was losing soil at the rate of more than 86 tons per acre per annum. This would mean the loss of the surface 7 inches in about 12 years. Such a close agreement with the figure of 14 years, as calculated from differences in magnesium saturation, suggests that magnesium saturation was maintained by truncation of the profile through erosion.

In the fallow subsoil, the magnesium saturation was 29.75 per cent in 1937. If this subsoil corresponds to the section in the bluegrass profile from 7 to 13 inches, then the mean magnesium saturation of these separate 1-inch layers would have been 28.69 per cent, or if the collection were made as a 7-inch sample it would have been 30.36 per cent. The fact that this subsoil was eroding at the rate of 7 inches in less than 17 years (13) indicates an approach toward a relatively constant degree of magnesium saturation with increasing depth in the profile below the thirteenth 1-inch layer, the limit of the study.

That magnesium saturation is higher in the subsoil than in the surface soil in another glacial drift profile was demonstrated in some studies by Harris and Drew (11). Though erosion produced a soil with a clay content almost twice as great in their studies, the exchange capacity had become correspondingly larger. The exchangeable magnesium increased slightly more than the clay content, to show increasing magnesium saturation in going from the surface to the subsoil. Other soil properties, such as exchangeable calcium, exchangeable potassium, total nitrogen, and organic matter did not increase accordingly. In some of these there were decided decreases. The exchangeable hydrogen increased much more than the clay content, suggesting that the magnesium saturation was maintained in the presence of increasing hydrogen saturation and of decreasing saturation by some of the other cations.

In the deep, virgin loess as it is more highly weathered under more intense climatic forces near Vicksburg, Mississippi,<sup>3</sup> than under the Missouri conditions concerned in this study, the exchangeable magnesium increases more than three-fold with depth in the solum. The calcium increases by only one eighth. At

<sup>3</sup> Reported by H. B. Vanderford in private communication.

a depth of 20 feet the exchangeable calcium is tenfold and the magnesium over sixfold that in the surface horizon. Here again, truncation of the profile to the extent of 12 inches would mean little change in the calcium saturation but more than doubling in concentration of exchangeable magnesium.

#### SUMMARY

The data presented in these studies, concerned with magnesium saturation of the soils under cropping with no erosion and in fallow soils with significant erosion, bring magnesium into the picture as a nutrient that is reduced significantly by cropping. They also suggest that erosion may have been serving in the past to hide what may be an impending serious deficiency in soil fertility. They point out further that the performances by bluegrass sod without soil treatment and by alfalfa and by rotation, both with lime and phosphate, ordinarily considered as soil-building effects, are decidedly depleting for magnesium, if decreasing degree of soil saturation of this nutrient may be taken as a criterion.

As our efforts in soil-building, particularly by liming, phosphating, cover cropping, and erosion prevention, serve with benefit to the active calcium and humus contents of the soil, they may be a detriment to the available magnesium supply. A liberal virgin store of magnesium in the more active form or a large stock in the mineral reserve may have been saving us from trouble in the past with respect to shortages of this nutrient. On some of the more highly developed soils of which the silt and sand fractions are very low in minerals other than quartz, and where such soils are now being maintained against erosion by conservation practices, it may not be long before the degree of magnesium saturation will be too low to guarantee good yields of crops. For some soils, as the Shelby silt loam used in this study, the practices in the past of using erosive systems of cropping, and of fallowing with its intensive erosion, may have prevented such troubles. Under intensive cropping with erosion prevention and the application of other fertilizer elements, however, the need for using magnesium as a soil treatment may soon become comparable to the present needs for calcium, potassium, and other fertilizer cations. The same fundamental principles underlying these in their plant and soil relationships will then help us to understand and manage the behavior of magnesium.

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# MICRODETERMINATION OF IRON BY THE MERCUROUS NITRATE METHOD<sup>1</sup>

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In a recent paper<sup>3</sup>, the author showed that the mercurous nitrate method for determining iron in the ferric state could also be used to determine small quantities of this ion. The method, however, was not rigorously examined as a micro-method. It is the purpose of this paper to show that the mercurous nitrate titration can be used satisfactorily on a microscale.

The method was tried out by titrating various quantities of ferric ammonium sulfate with 0.00467 *N* mercurous nitrate using 1 ml. of 40 per cent ammonium

TABLE 1  
*Recovery of iron by the mercurous nitrate method*

12 <i>N</i> HCl	Fe TAKEN	Fe RECOVERED	ERROR
ml.	mgm.	mgm.	mgm.
0	0.569	0.559	0.010
0	1.116	1.115	0.001
0	1.116	1.112	0.004
0	1.116	1.112	0.004
0	1.116	1.115	0.001
0	1.674	1.683	0.009
0	2.232	2.226	0.006
0.1	1.116	1.125	0.009
0.2	1.116	1.112	0.004
0.3	1.116	1.107	0.009
0.4	1.116	1.107	0.009
1.0	1.116	1.112	0.004
5.0	1.116	1.113	0.003

thiocyanate as an indicator. The titration was performed in a volume of 20 ml., and the disappearance of the red color was used as the endpoint. In order to determine the effect of the chloride ion and of acidity, some of the titrations were performed in the presence of various amounts of hydrochloric acid.

The data, shown in table 1, indicate that the microtitration can be used to determine as little as 0.5 mgm. iron with an error of less than 10  $\mu$ gm. Though large concentrations of chloride ion interfere in the macrotitration, there is no interference of this ion on a microscale and hence hydrochloride acid may be used to dissolve the sample.

<sup>1</sup> Journal Series paper of the New Jersey Agricultural Experiment Station, Rutgers University, department of soils.

<sup>2</sup> Now with the Tennessee Valley Authority, Wilson Dam, Alabama.

<sup>3</sup> Kunin, R. 1942 Determination of iron in soils and silicates by the mercurous nitrate method. *Soil Sci.* 53: 211-214.



# GENESIS OF A CLAYPAN SOIL: I

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This paper has a dual purpose: first, it describes a method for interpreting data obtained by soil analyses and, second, it presents in the light of this method the results of investigation of a claypan soil, Dayton silt loam, with particular reference to the origin of the claypan. Thus, the first part of the paper deals with the theory of the method and the second with its application to the interpretation of soil analyses.

## THE METHOD OF INVESTIGATION

The authors are aware that the material used for demonstrating the method is not entirely satisfactory and that the method is not perfect. They assume, however, that the principles upon which the method rests are sound and that the results thus obtained, even though they are not precise, give a better view of the changes of the parent material during its transformation into the soil.

Interpretation of the results of soil analyses is difficult because in most instances we do not know the exact composition of the original material in each soil horizon and also because of the concurrence of various processes in the same horizon. The data obtained by soil analyses show the summary effect of all these processes without sufficient, if any, information about the specific result of each individual process. Indeed, the soil is the product of integration of all factors which affect its formation. An adequate explanation of its origin, however, cannot be based on the summary effect, but requires a careful study of all the additives that comprise the sum. This may be accomplished by an appropriate mathematical analysis of the data obtained in the laboratory.

Usually these data present the composition of different soil horizons in percentages of their constituents. In other words, they refer to a certain amount, as for example, a gram or 100 gm. of the whole material of the corresponding horizon. A conclusion about the origin of the soil usually is based on differences in composition of the various horizons. A gram of material from one horizon, however, rarely represents the equivalent of a gram of material from another horizon. One might include more humus, combined water, carbonates, or other incorporated substances so that one gram of this material is equivalent to less than a gram of the original material. Or on the other hand, a gram of material from a strongly leached horizon would be equivalent to more than a gram of original material. Thus, the data on composition of different soil horizons usually do not refer to a common basis and are not directly comparable. The differences in composition of various horizons which may be shown by these data are only apparent. Indeed, an adequate conclusion cannot be drawn by de-

<sup>1</sup> Bureau of Plant Industry, Agricultural Research Administration.



ductive reasoning alone, based on apparent differences, but requires an inductive study based on facts which might be revealed by a critical analysis of the data obtained in the laboratory.

The proposed method for such a mathematical analysis is still rather crude, especially because we lack definite knowledge of certain important aspects of soil formation and are compelled to infer whenever the necessary data are not available. It is hoped that eventually the field of inference will shrink to the vanishing point and the method will be improved. The outline of the method and its underlying principles follows.

### *Migration and segregation*

Assuming that the soil develops from a sufficiently homogeneous parent material, one must also assume that the individual characteristics acquired by different horizons of such a soil are due to certain changes of the original material and that these changes in any given horizon are different from those which take place in the other horizons.

Presumably these changes begin with the decomposition of certain minerals, which leads to changes in the petrographic composition of the original material. The further modifications of this material in the different horizons depend especially upon the fate of the products of decomposition. Some changes are due to the recombination in place of the constituents of the original material without their being moved from one horizon to another, whereas other changes depend entirely upon the translocation of various substances which might have been set free to move by the decomposition. The processes of recombination in place will be referred to hereafter as *segregation*, and the process accompanied by the transfer of any substance either from one horizon to another or out of the soil, as *migration*.

Both migration and segregation are accompanied by changes in content of various constituents in certain parts of the soil. In the case of migration these "parts" refer to the different horizons, whereas in the case of segregation the parts usually represent either different mechanical fractions, such as silt, clay, and colloid, or certain special formations, such as concretions and the matrix in which they are formed.

The changes in chemical composition of the parent material which are caused by migration are indicated by the difference in composition of the *whole materials* from various horizons. On the other hand, segregation does not change the content of individual constituents in the whole material in which it takes place. A material thoroughly modified by recombination of its ingredients may have essentially the same general composition as the unmodified material. Thus, the effects of segregation cannot be shown by analysis of the whole soil; they might be indicated, however, by the differences in amount and composition of the various mechanical fractions in different soil horizons.

The decrease in content of any constituent in a given part of the soil due to either migration or segregation naturally is accompanied by a relative increase in content of other constituents, and *vice versa*, the increase in content of migrants

or segregants is accompanied by a decrease in content of stable constituents. Thus, the true or *absolute* losses or gains which might have been caused by either process must be distinguished from the accompanying *relative* or *apparent* losses and gains.

Modification of the original material in any soil horizon seldom is due entirely to either migration or segregation. Moreover, it is not always clear whether a particular loss or gain is absolute or only apparent. The failure to recognize the real character of the process and the true significance of the data frequently is the source of wholly untenable conclusions as to various aspects of the origin and character of the soil.

During the last few decades considerable attention has been given to migration, which was considered as the major factor in the development of the soil profile. Overrating the importance of migration has led to undue neglect of the role of recombinations in place, which most likely is greatly underestimated. The proposed method is nothing more than an attempt to find out the means for a reasonable evaluation of the effects produced by either process separately.

This method consists of a certain integration of mechanical, mineralogical, and chemical soil analyses, the latter including analyses of the whole materials and of various mechanical fractions individually. Since the method deals with the data obtained by analyses of many different materials, such as the whole soil, silt, clay, and colloid, each of them from various soil horizons, it is necessary that all data be referred to a common basis.

In this paper 100 gm. of the unmodified parent material is taken as the point of reference and the basis of calculation. It is assumed that the entire soil profile has been developed from a relatively uniform material. Complete uniformity of the parent material would be an ideal condition, which does not exist in nature. Relative uniformity, therefore, is the best existing condition under which a comparison of the modified and unmodified materials is possible, provided, however, that changes due to the modification are sufficiently greater than the inherent variations in composition of the original material. Obviously, the derived data cannot be absolute; they might reveal the general character of modification but give only an approximate quantitative expression of it.

Another prerequisite of the method is that some constituent of the original material be relatively stable and migrate but little, although it may undergo various changes in mode of combination. Again, it would be ideal if it were possible to prove that some constituent occurring in sufficient quantity is absolutely immobile. It is difficult to conceive, however, that any constituent would be so stable in a medium which is attacked continuously by weathering. Again we are compelled, therefore, to base the calculation on a relative stability of some constituent which is least likely to be moved, assuming that the changes in content of this constituent are so small in comparison with the changes in content of other less stable substances that they can be neglected without causing too grave an error.

The method consists of the following calculations: First, the data obtained by analyses are expressed in exact percentages of the material free of any incor-

porated substances, such as humus, combined water, or free carbonates; second, the data obtained by the first calculation are recalculated upon a parent material quotient ( $Q$ ); third, the data obtained by the second calculation are recalculated upon a volume factor ( $v$ ); fourth, the data obtained by chemical analysis and corrected by the first calculation are recalculated upon a basis obtained by mechanical analysis previously recalculated upon the parent material quotient. The purpose and method of the first operation need no explanation. The principles of other calculations are described as follows.

### *Parent material quotient*

As used in this paper the *parent material quotient* ( $Q$ ) represents one-hundredth of the gram-equivalent of the soil. The *gram-equivalent* is the amount of a modified material in any soil horizon that represents a residue or modification of a definite amount, such as 100 gm. of the original material. For example, suppose that 100 gm. of the original material in the A horizon is reduced by leaching to 86 gm. of residue, whereas an equal amount of the same material in the B received 2 gm. of material by illuviation. The gram-equivalents in the A, B, and C horizons of such a soil are 86, 102, and 100 gm. and their parent material quotients are 0.86, 1.02 and 1.00, respectively. Obviously, 100 gm. of the whole material in the A represents the residue of about 116.3 gm. of the original material, whereas 100 gm. of material in the B is the product of modification of about 98 gm. of such a material.

The value of the gram-equivalent can be obtained by calculating the results of chemical analysis by using a constant factor ( $K$ ) represented by any constituent of the original material that is sufficiently stable in the environment in which this material undergoes modification. For example, suppose that silica is relatively stable and does not move from one horizon into another. If the parent material is sufficiently uniform, then 100 gm. of it in each horizon contains about an equal amount of silica, and, since the silica does not migrate, the same amount of it must remain in the equivalent amount of the modified material. Thus, the content of the stable constituent in 100 gm. of the original material might be taken as the constant factor. The amount of the whole soil in any horizon which contains as much stable constituent as does 100 gm. of the parent material represents the gram-equivalent of this horizon.

The parent material quotient ( $Q$ ) is obtained by dividing the percentage of the constant constituent in the original material by the percentage of the same substance in the modified material. For example, suppose that the content of silica in the A and C horizons is 76.16 and 65.44 per cent, respectively. Then  $Q$  for the A horizon is 0.8592 and the gram-equivalent is 85.92. (The data given indicate that in the A horizon 76.16 gm. of silica is associated with 23.84 gm. of other substances. Therefore 65.44 gm. of silica representing the constant factor is tied with 20.48 gm. of other material and the sum total of these amounts, i.e., 65.44 + 20.48 makes up the gram-equivalent.)

The difference between the gram-equivalent and 100 represents the difference between the sum total of the true losses and the sum total of the true gains which

are due to the migration of various constituents. The data in our example indicate that the combined loss in the A exceeds the combined gains, if any, by 14.08 gm. per 100 gm. of the original material.

The true loss or gain of any particular constituent (subject to the limitations mentioned) can be obtained by recalculating the percentage of this substance upon the parent material quotient and subtracting the result from its percentage in the original material. For example, if the content of alumina in the A and C horizons of the soil in the previous example is 13.16 and 18.06 gm., respectively, then the true loss of it from the A is  $18.06 - 13.16 \times Q$  or 6.74 gm. per 100 gm. of the parent material. The general formula employed in this calculation is as follows:

$$x = So - \frac{Sh \cdot Ro}{Rh} \quad (1)$$

in which

$x$  is the true loss or gain of a given substance,  
 $So$  is the percentage of this substance in the original material,  
 $Sh$  is the percentage of the same substance in a given soil horizon,  
 $Ro$  is the percentage of the constant substance in the original material,  
 $Rh$  is the percentage of this constant substance in a given horizon.

$$\frac{Ro}{Rh} = Q.$$

Obviously, the various constituents of the residual material as well as their losses or gains calculated on the parent material quotient are no longer expressed in percentages of the whole soil but are given in grams per 100 gm. of the original parent material.

The constant factor ( $K$ ) might be represented by a certain immobile constituent such as silica or alumina, or it might be represented by a certain mechanical fraction such as sand. Again, it may be represented by a certain mineral such as primary quartz or muscovite. The value of the gram-equivalent should be checked against all available data.

#### *Volume factor*

The true losses or gains of various constituents refer to a definite amount, such as 100 gm. of the original material, and do not represent the total losses or gains of these substances from the entire soil horizons. On this basis, the true loss of any given substance in one soil horizon cannot be compared with the gain of the same material in another horizon. Balancing is possible only between the total loss and total gain which might be obtained by calculating the true losses and gains upon the volume factor ( $v$ ) that represents the index of the thickness of the corresponding soil horizon.

For example, consider a soil in which the  $A_2$  and B horizons are 8 and 12 inches thick, respectively. Suppose that the true loss of iron oxide in the  $A_2$  is 3.39 gm. per 100 gm. of the parent material, whereas the true gain of this oxide in the B is 1.75 gm. for the same amount of parent material. Consider a column of this

soil of such a thickness that it contains 100 gm. of parent material per vertical inch. If such a column extends throughout the  $A_2$  and B horizons, then the total loss of iron oxide in the  $A_2$  and the total gain in the B are 27.12 and 21.00 gm., respectively, per column of a given cross section. (Such a column will be referred to hereafter as column  $Z$ . The symbols  $Za$ ,  $Za_2$ ,  $Zb$ , etc. will refer to the parts of column  $Z$  extending throughout the A,  $A_2$ , B, etc. horizons, respectively). These data show that not all the iron oxide which was shifted from the  $A_2$  is retained in the B horizon.

Indeed, the foregoing example is much simplified. It must be borne in mind that the thickness of the soil horizons is measured on modified materials and that a vertical inch of column  $Z$  composed of the original material does not necessarily correspond to 1 inch of the columns  $Za$ ,  $Za_2$  and  $Zb$ . A column  $Z$  of the fresh parent material has a uniform cross section and density from the top to the bottom. This, however, is no longer true after the development of the soil horizons. The column may shrink or its density may decrease in the leached horizon, whereas it may expand or become more compact in the illuvial horizon. Thus, the precise value of  $v$  does not depend exclusively upon the thickness of the soil horizon but is affected by several other conditions such as porosity of the various horizons and specific gravity of its solid matter. No attempt is made at this point to estimate exactly the so-called total losses and gains. The purpose of calculation upon the volume factor as made in this paper is simply to give some idea of the approximate magnitude and the general trend of migration and to show the general character of distribution of the migrant substances. For present purposes we will assume that index  $v$  might be represented by the thickness of the corresponding horizon corrected according to the parent material quotient.<sup>2</sup>

A precise determination of the total losses and gains is made difficult also by the lack of clear-cut boundaries between the adjacent horizons. The transitional sections of the soil profile in which the characteristics of the upper and lower horizons are blended may suffer a loss in one part and incur a gain of the same substance in another. Obviously, these losses and gains mask each other, and only the difference between them might be depicted. Therefore, the "total" losses and gains calculated for the entire soil profile might be somewhat less than they really are.

### *Calculating the results of segregation*

Determining the results of segregation requires first calculating the mechanical analyses upon the parent material quotient. For example, suppose that the content of sand, silt, and clay in the B horizon is 2.6, 48.7, and 48.7 per cent, respectively, and that  $Q$  for this horizon is 1.0154. The content of sand, silt, and

<sup>2</sup> The differences in specific gravity of the whole materials in various soil horizons depend especially upon the differences in content of organic matter and combined water. Since our calculations deal only with water-free mineral matter, the significance of this factor may be reduced by correction of the index  $v$  according to the loss of ignition. Further corrections of the index must be made according to the parent material quotient and the change of porosity.

clay in the gram-equivalent will be 2.64, 49.45, and 49.45 gm., respectively. If 100 gm. of the parent material consisted of 2.2 gm. of sand, 74.8 gm. of silt, and 23.0 gm. of clay, then modification of this material in the B horizon was accompanied by the loss of 25.35 gm. of silt and the gain of 26.45 gm. of clay and 0.44 gm. of sand (most likely in the form of concretions). The excess of gains over loss, equal to 1.54 gm., is most likely due to illuviation.

The next step consists of calculating the chemical analyses of various fractions upon the results obtained by the first operation. For example, suppose that the content of silt in 100 gm. of the parent material and in its gram-equivalent in the B horizon is 74.8 and 49.45 gm., respectively. Suppose that the content of silica in the silt from the parent material and from its modification in the B is 68.09 and 73.49 per cent, respectively. These data indicate that the silt in 100 gm. of the parent material contained 50.93 gm. of silica, whereas the residual silt in the product of modification of the same amount of this material in the B retained only 36.34 gm. of silica. Thus, modification of the parent material in the B was accompanied by the loss from the silt of 14.59 gm. of silica, which makes up about 28.6 per cent of  $\text{SiO}_2$  that was present in the silt of the original material.

Now, suppose that the content of the clay in 100 gm. of the parent material and in its gram-equivalent in the B is 23.0 and 49.45 gm., respectively and that the content of silica in the clay from the C and B horizons is 56.45 and 55.96 per cent, respectively. The content of silica in the clays from 100 gm. of the parent material and its gram-equivalent in the B is 12.98 and 27.67 gm., respectively, which indicates a gain of silica in the clay in the B horizon equal to 14.69 gm. per 100 gm. of the parent material.

Assuming that the difference between the loss of silica from the silt (14.59 gm.) and the gain in the clay (14.69 gm.) is due to analytical error<sup>3</sup>, one may conclude that modification of the parent material in the B horizon of this soil was accompanied by the transfer of about 14.64 gm. of silica from silt to clay. This amount makes up about 22 per cent of the total silica in the whole parent material. This is an example of modification of the original material by the recombination of its constituents *in place*. Indeed, it is not inferred that all this silica was set free by a complete chemical breakdown of the silt minerals and recombined in the secondary clay minerals. It is quite possible that a part of the transfer was due to the physical breakdown of the silt particles into fragments less than  $2 \mu$  in diameter.

This calculation is based on the same assumptions used in calculating the true losses and gains and, therefore, is subject to the same limitations. Since it involves the data on composition of different fractions of the soil, however, it offers an opportunity to check on the validity of the underlying assumptions. For example, in calculating the data used throughout this discussion, it was

<sup>3</sup> This difference may be considerably greater than that in our example. This is to be expected, when one considers that the derived data are obtained by calculating the results of eight different analyses, including separation of the silt from the B and C materials, separation of the clay from these materials, and chemical analyses of the silts and clays thus obtained.

assumed that the soil was developed from a relatively uniform parent material and that silica was relatively stable throughout the soil profile. Based on these assumptions, the parent material quotients were determined and the loss of silica from the silt in the B horizon was calculated. On the assumption that this loss is due to the transfer of silica from the silt to the clay, it can be calculated that the content of silica in the clay of the B horizon should be 55.75 per cent. The chemical analysis shows 55.96 per cent. Such a correlation hardly could be expected if any of the assumptions were wrong.

The general formula employed for calculating the true losses and gains of any constituent of any mechanical fraction in a given soil horizon is as follows:

$$x = \frac{So \cdot Fo - Sh \cdot Fh \cdot Q}{100} \text{ gm.} \quad (2)$$

in which

- $x$  is the amount of substance  $S$  lost or gained in fraction  $F$  in a given soil horizon  $h$  (in grams per 100 gm. of the original material),
- $So$  is the percentage of this substance in fraction  $F$  of the parent material,
- $Sh$  is the percentage of the same substance in the same fraction of a given horizon,
- $Fo$  is the percentage of fraction  $F$  in the parent material,
- $Fh$  is the percentage of the same fraction in a given horizon,
- $Q$  is the parent material quotient.

If the results of this calculation show that the loss of a given constituent from one fraction is more or less equal to the gain of the same substance in all other fractions, then it might be concluded that virtually all the material released from one fraction is incorporated in the others. If the loss is considerably greater than the gain, then the excess of the released substance most likely has been leached out from the horizon. On the other hand, if the loss is considerably less than the gain, then the excess must have come from outside this horizon. The differences, however, must be considerable. Smaller differences might be due to the inevitable defects of analyses and calculations.

The application of the method to Dayton silt loam involves the assumptions of a sufficiently uniform parent material and relative stability of silica. It is believed that any deviations from these assumptions are insignificant as compared to the changes in composition of the original material which are due to the development of the soil. Although it is realized that the data derived by these calculations do not give an exact quantitative expression of the soil-forming processes, it is felt that they do give an approximate evaluation of the different phases of the processes.

#### MORPHOLOGY, MECHANICAL AND CHEMICAL COMPOSITION OF DAYTON SILT LOAM

##### *Morphology*

Dayton silt loam belongs to a group of intrazonal soils which develop in shallow depressions, on low terraces, and in other poorly drained areas scattered throughout the podzol and chernozem zones. The outstanding characteristics of these



A



B

FIG. 1A. A PROFILE OF SOLODI IN VORONEZH PROVINCE, U.S.S.R. (AFTER POPOV)  
FIG. 1B. A PROFILE OF DAYTON SILT LOAM IN WILLAMETTE RIVER VALLEY, OREGON



soils are a strong bleaching of the  $A_2$  horizon and the development of a dense claypan which represents the B horizon.



FIG. 2. A VIEW OF THE WILLAMETTE VALLEY, OREGON, SHOWING A FLAT AREA OCCUPIED BY THE DAYTON SOILS



FIG. 3. NATIVE VEGETATION ON DAYTON SILT LOAM

The site of profile 808. The area has been pastured for many years but never plowed

This general type of soil develops from different parent materials, including recent alluvium, calcareous loess, glacial drifts, and various residual materials,

and is formed under a wide range of rainfall, from less than 15 to more than 40 inches. Such a variety of parent materials and climate suggests that some local condition, such as the impeded drainage of the areas in which they occur, is the major factor in the development of soils of this type.

Originally, these soils were described by Glinka (8) and his co-workers as meadow podzols, glei-podzolic soils, and steppe-podzols. Later, Popov (12), Gedroiz (6, 7), and others introduced the popular name *solodi* as a substitute for steppe-podzols and developed a hypothesis for their genesis. Gedroiz (6) holds that solodization differs from podzolization in that the former process is accompanied by an accumulation of colloidal silica in the  $A_2$ , whereas no such accumulation takes place in true podzols.

Morphological characteristics of Dayton silt loam are essentially the same as those of typical *solodi*. In figure 1 are shown a profile of *solodi* in Voronezh Province in the U.S.S.R. and a profile of Dayton silt loam in Oregon. The purpose of this investigation was to elucidate the genesis of the Dayton soil, especially the formation of the claypan.

Accumulation of clay in the B horizon characterizes a great many different soils. Not all B horizons that are enriched in clay are regarded as true claypans. The difference between the true claypan and the clayey B horizon, however, might be only quantitative, depending on the difference in intensity of the formation of clay in various soils.

Usually the accumulation of clay in the B horizon is ascribed to the illuviation of the clay or colloid from the upper horizons. Brown *et al.* (3) conclude that their data obtained by analyses of certain claypan soils demonstrate the enrichment of the lower strata by illuviation, that the translocation which occurred is essentially of colloid only, and that the colloid as a whole is translocated from the surface downward by dispersion and eluviation. This interpretation of the formation of the heavy B horizon is not new. Earlier Hissink (9) asserted that under certain conditions the suspended particles of clay including the sols of iron oxide, silica, and alumina are carried downward by percolating water together with various dissolved substances. According to Glinka (8), podzolization is due to the eluviation of the unstable organic sols and fine mineral suspension from the upper horizons and their precipitation in the B horizon.

The Dayton soils, of which the silt loam is the most common, develop on broad and level terraces of the Willamette River Valley in western Oregon (fig. 2). Before the breaking of the virgin sod, most if not all of this land was occupied by open sedge meadows with scattered small clumps of oak and alder and small shrubs of willow and wild roses (fig. 3). The climate of this region is characterized by a decided winter concentration of precipitation. The mean annual rainfall is about 40 inches, of which more than 70 per cent, or about 30 inches, falls during the winter and only about 9 per cent, or about 4 inches, during the summer.

Because of the lack of adequate surface drainage and of the water-tight subsoil, the Dayton soils become saturated soon after the beginning of the rainy season, usually in the latter part of October, and remain in this condition until

late in the spring. Water covers large tracts of slightly depressed land and stands on the surface for weeks, even months. The dry and rather hot spells during the summer, however, are sufficiently long for a thorough desiccation of the soil.

The parent material of the Dayton soils is the relatively recent, well-assorted, silty alluvium, entirely free of gravel and almost free of coarse sand. The upper layer of this material, which ranges in thickness from about 4 to more than 10 feet, presumably was uniform in mechanical and chemical composition before the development of the soil profile. The results of analyses of three samples of this material taken in different places are presented in table 1.

Below the upper layer the material gradually becomes somewhat coarser as a result of an increase of silt and fine sand. In some places, however, the upper silty alluvium ends abruptly and rests on a bed of either out-washed sand or

TABLE 1

*Mechanical and chemical composition of the parent material of Dayton silt loam*

	PROFILE A	PROFILE B	PROFILE C	AVERAGE OF THREE PROFILES
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Sand (2.0-0.05 mm.).....	2.1	3.1	2.0	2.4
Silt (0.05-0.002 mm.).....	74.8	70.3	74.6	73.2
Clay (<0.002 mm.).....	23.0	26.3	23.6	24.3
SiO <sub>2</sub> .....	62.70	63.40	62.40	62.83
Al <sub>2</sub> O <sub>3</sub> .....	17.30	16.00	16.50	16.60
Fe <sub>2</sub> O <sub>3</sub> .....	7.00	7.30	7.90	7.40
CaO.....	2.09	2.17	2.27	2.18
MgO.....	2.04	1.96	1.89	1.96
K <sub>2</sub> O.....	1.84	1.48	1.70	1.67
Na <sub>2</sub> O.....	1.25	1.31	1.32	1.29
MgO.....	0.13	0.17	0.15	0.15
TiO <sub>2</sub> .....	1.21	1.16	1.22	1.20
P <sub>2</sub> O <sub>5</sub> .....	0.25	0.39	0.38	0.34
Ignition loss.....	4.35	4.04	4.27	4.22

stratified gravel. So far as we know, the boundary between the silty layer and gravel seldom is less than 10 feet below the surface.

Twenty-eight profiles of Dayton silt loam and a number of profiles of the soils related to it were examined in Benton, Polk, Linn, and Yamhill Counties, Oregon. According to our data, the profile of Dayton silt loam is as follows:

The A horizon averages 17 inches and ranges from 8 to 33 inches in thickness. The extremes, however, are rather rare; commonly the thickness of the A ranges between 14 and 20 inches. This horizon is characterized by a very light gray color, which is due to the white "podzolic flour" that thoroughly pervades the entire horizon but is especially abundant in its middle and lower parts, thus marking the strongly bleached A<sub>2</sub> subhorizon. In the moist condition the material of the A is mellow to moderately plastic; on drying, however, it cakes into a massive and rather hard crust. The lower boundary of the A usually is very sharp and smooth (fig. 4). Numerous burrows of earthworms, partly filled with casts and partly empty, penetrate the whole horizon, and some of them extend into the B.

The B horizon averages 14 inches and ranges from 8 to 23 inches in thickness. In only a few places, however, is it less than 12 or more than 20 inches thick. It is very dark olive-gray or almost black and is compact. On drying it breaks into large and roughly prismatic clods (figs. 4 and 5) which range from 2 to about 4 inches in diameter and extend from the top to the bottom of this horizon. The clods are very hard; their tops are roughly rounded (fig. 6). The wide and nearly vertical cracks which separate the clods extend throughout the B and the largest of them continue to some depth into the C. Most of the cracks, however, end near the base of the B; consequently the adjacent prisms are not separated from each other in the lower part of the horizon. The walls of the cracks usually are coated with

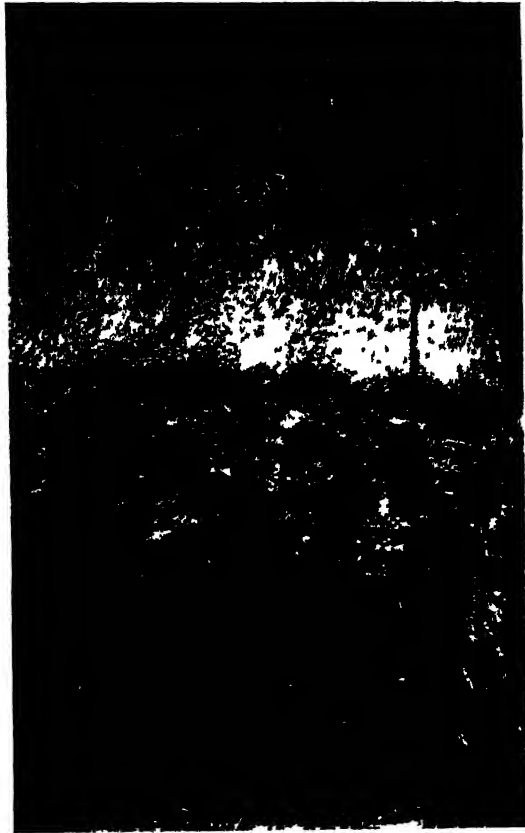


FIG. 4. PROFILE OF DAYTON SILT LOAM (No.

dark shining films, which are especially prominent in the cracks extending into the C horizon. After sufficient wetting, the prisms swell, and the cracks close. The entire horizon becomes almost watertight. In this condition the material of the B is exceedingly sticky. The lower boundary of the B is indistinct and more or less wavy.

The C horizon has a light olive-gray color with a pronounced yellow tint which becomes stronger with depth. Usually the upper part of the C extending to about 50 or 60 inches from the surface is mottled with rusty stains and minute dark brown and black specks.

A large number of black or brown iron-manganese concretions are formed throughout the solum of all Dayton soils. The concretions are especially num-



FIG 5 COARSE PRISMATIC STRUCTURE IN THE B HORIZON OF DAYTON SILT LOAM



FIG 6 ROUGHLY ROUNDED TOP OF THE PRISMS IN THE B HORIZON OF DAYTON SILT LOAM

Material of the  $A_2$  was blown away by an air pump

erous and large in the  $A_2$  horizon. These concretions are described in detail elsewhere (5).

It will be noted that the lower limit of the thickness of the A and B horizons

is placed at about 8 inches. This limit is arbitrary. As a matter of fact, there is a continuous series of soils ranging from the one in which the  $A_2$  is more than 2 feet thick and the claypan is virtually absent to another having a claypan more than 3 feet thick and only an incipient, if any,  $A_2$ . It was noticed, however, that the  $A_2$  and B horizons acquire all their specific characteristics only when they are not less than about 8 inches thick. If the A horizon is thinner than this, its color, podzolic flour, and concretions are less conspicuous; its texture is heavier; and its lower boundary is less distinct. If the B horizon is thinner, it usually is lighter in color, is somewhat coarser in texture, and on drying breaks into small irregular lumps instead of prisms.

The soils with a strongly developed claypan and an incipient  $A_2$  and especially those without the claypan and with a strongly developed  $A_2$  are less common than the soils in which both horizons are fully developed. Nevertheless, their existence suggests that formation of the claypan in all these soils is not merely a consequence of eluviation of the  $A_2$  and an accumulation of the migrant colloids in the B: it might take place independently of the development of the leached horizon above it.

Samples of Dayton silt loam were collected for analyses in three different places. After a preliminary study of these samples one profile (No. 808) was selected for detailed study. It was taken in a poorly drained, continuously pastured sedge meadow, presumably never plowed, in Linn County, Oregon; T. 14S; R. 4W; SW $\frac{1}{4}$  of SE $\frac{1}{4}$  of Section 12 at an elevation of about 240 feet above sea level. A brief description of this particular soil profile follows:

- A<sub>1</sub> 2-inch thick, light gray silt loam.
- A<sub>2</sub> 8-inch thick, very light gray silt loam with numerous concretions.
- A<sub>2</sub>-B 4-inch thick, dark gray crumbly silty clay; transitional between the A<sub>2</sub> and B.
- B 12-inch thick, very dark gray, almost black clay broken into coarse prismatic clods.
- B-C 8-inch thick, olive-gray silty clay to silty clay loam slightly mottled with yellow stains; transitional between B and C.
- C light yellowish gray silt loam; uniform as far as examined (to a depth of about 9 feet).

The methods of determining the various constituents and properties of the soil samples were essentially those in general use by the Division of Soil Chemistry and Physics, U. S. Department of Agriculture. Mechanical analyses were made by the pipette method of Olmstead *et al.* (11) except for the added changes mentioned by Knight (10). The chemical composition of the whole soil and of the silt, whole clay, and colloids separately was determined according to the procedure outlined by Robinson (13). The hydrogen electrode described by Bailey (1) was used in determining the pH. The colloids were extracted according to the procedure of Brown and Byers (2). No dispersion agent was used. The iron-manganese concretions were studied and analyzed separately, and the results have been reported elsewhere (5). The base-exchange capacity and the exchangeable bases were determined at pH 7.0, normal ammonium acetate being used as the replacing agent. Free iron oxide was determined by

a modification of the method of Drosdoff and Truog (4). Gedroiz' method of extraction with KOH was used to determine the so-called amorphous silica.

Only a part of the data obtained are presented in this paper. All data included here are calculated in exact percentages of the material free of organic matter and combined water.

### *Mechanical composition*

Table 2 presents the mechanical composition of the principal horizons of Dayton silt loam. The percentage of sand shown in this table was determined by difference, i.e., 100 minus the percentages of silt and clay. This sand includes all particles ranging from 0.05 to 2.0 mm. in diameter. A small quantity of particles larger than 2 mm. has been separated from the soil in the preparation of the sample for analysis and disregarded in the calculation. Examination of the sand under a microscope showed that a large part of it consists of concretions. It has been found (5) that almost all particles larger than 1 mm., about

TABLE 2  
*Mechanical composition of Dayton silt loam*  
Calculated on basis of soil free of organic matter

LABORATORY NUMBER	HORIZON	DEPTH	SAND	SILT	CLAY
		<i>inches</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
C-4226	A <sub>1</sub>	0-2	3.9	82.7	13.4
C-4228	A <sub>2</sub>	6-10	3.8	79.5	16.7
C-4229	A <sub>2</sub> -B	10-14	4.7	70.5	24.8
C-4231	B	18-22	2.6	48.7	48.7
C-4233	B-C	26-30	1.5	59.4	39.1
C-4236	C	42-50	2.2	74.8	23.0

70 per cent of particles ranging from 1 to 0.5 mm., about 50 per cent of those ranging between 0.5 and 0.25 mm., and about 30 per cent of those smaller than 0.25 mm. are concretions or their fragments. The concretions are formed by the cementation of the soil into hard secondary aggregates. Such a cementation binds a certain amount of primary sand, silt, and clay into larger, complex grains. Concretions are especially numerous in the A<sub>2</sub> horizon, in which they may comprise more than 10 per cent by weight of the whole material with as much as about two thirds of their bulk composed of concretions larger than 2 mm. A considerable part of these large concretions was separated from the sample taken for analysis. The less firm concretions undoubtedly were crushed during the preparation of the soil for analysis. Nevertheless, the quantity of concretions or their fragments in the A<sub>2</sub> horizon may account for about half of the material that is classed as sand. Perhaps a higher content of sand in all parts of the A horizon as compared with that in the B and C is due to the presence of concretions. It is not unlikely that if all the concretionary material were excluded from the sand, the content of sand would be more or less uniform

throughout the profile and would amount to about 2 per cent of the whole material.

Silt and clay combined make up from 95.3 to 98.5 per cent of the whole soil in different horizons, the smaller amount being in different parts of the A in which some amount of silt and clay is tied up in the concretions. Thus, one may assume that the quantity of silt and clay is virtually the same throughout the soil profile. The silt to clay ratio in different horizons, however, ranges from about 5 to 1 in the  $A_2$  to 1 to 1 in the B. The parent material contains about three times as much silt as clay; in the  $A_2$  the content of silt rises to about five times that of clay, whereas in the B there is just as much clay as silt.

At first glance, the distribution of silt and clay in the various horizons of this soil may suggest the migration of a large amount of clay from the A horizon into the B. It will be remembered, however, that the changes in content of different fractions in various horizons are only apparent. It will be shown in table 5 that the residue of 100 gm. of the parent material, i.e., its gram-equivalent in different horizons, ranges from 85.92 to 101.54 gm. Assuming 100 gm. of the original material which consists of 2.2 gm. of sand, 74.8 gm. of silt, and 23.0 gm. of clay as a common basis<sup>4</sup> and having determined the amounts of sand, silt, and clay in each equivalent, we may calculate the true losses and gains of each fraction in various horizons. For example, the residue of 100 gm. of the original material in the  $A_2$  amounts to 87.7 gm. This residue contains 16.7 per cent of clay. Thus, the amount of clay in 87.7 gm. of this residue is 14.65 gm. This residue is the product of modification of 100 gm. of the parent material which contained 23 gm. of clay. The true relative loss of clay in the  $A_2$  is, therefore,  $23.00 - 14.65$  or 8.35 gm. The  $A_2$  is 8 inches thick and its volume factor is about 9. Thus, the total loss of clay from the  $A_2$  is about 75 gm. per column  $Za_2$ . The results of these calculations are given in tables 3 and 4. The derived data in these tables show an absolute increase in content of sand in the  $A_2$  and B horizons, which most likely is due to the formation of hard concretions. Indeed, this increase represents only a part of the concretions that were not crushed in the preparation of the soil for analysis or separated from the soil sample.

The data in table 4 show that the  $A_1$ ,  $A_2$ , and A-B horizons together have lost about 106 gm. of clay and about 108 gm. of silt. Assuming that the loss of silt was due to its decomposition and that about 20 gm. of silt and clay (included in general losses) were cemented in concretions in place, one may calculate that the sum total of loss from the A amounts to about 192 gm. per column  $Za$ , which originally weighed 1,590 gm.

The total gain of clay in the B and B-C horizons, however, amounts to about 445 gm. (to which should be added about 50 gm. of clay gained in the layer under-

<sup>4</sup> The material having such a composition is represented by the sample that was taken at a depth of 42 to 50 inches from the surface of the soil. On the basis of data given in table 1 it is assumed that this sample represents the unmodified parent material. Another sample of the same soil taken from a depth of 34 to 42 inches and designated in the field as C contains 30.2 per cent of clay and 68.0 per cent of silt. Thus, mechanical analysis shows that this sample represents the lowermost part of the transitional B-C horizon.



neath the B-C). This indicates that a combined loss of silt and clay from the A horizon makes up less than 40 per cent of the gain of clay in the B and that the other 60 per cent of the accumulated clay was formed in place. The data in table 4 show the loss in the B horizon of about 416 gm. of silt which apparently was decomposed, the products of decomposition being intermingled with the original clay and the clay products transferred from the A horizon. This mixture

TABLE 3

*Relative losses or gains of the sand, silt, and clay in different horizons of Dayton silt loam*  
Calculated on basis of soil equivalents

HORIZON	SOIL EQUIVALENT	CONTENT IN EQUIVALENT			LOSS OR GAIN			SUM TOTAL OF LOSSES	SUM TOTAL OF GAINS	DIFFERENCE
		Sand	Silt	Clay	Sand	Silt	Clay			
	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.
A <sub>1</sub>	85.92	3.35	71.06	11.51	+1.15	-3.74	-11.49	-15.23	+1.15	-14.08
A <sub>2</sub>	87.70	3.33	69.72	14.65	+1.13	-5.08	-8.35	-13.43	+1.13	-12.30
A <sub>2</sub> -B	89.34	4.20	62.98	22.16	+2.00	-11.82	-0.84	-12.66	+2.00	-10.66
B	101.54	2.64	49.45	49.45	+0.44	-25.35	+26.45	-25.35	+26.89	+1.54
B-C	101.27	1.52	60.15	39.60	-0.68	-14.65	+16.60	-15.33	+16.60	+1.27
C	100.00	2.20	74.80	23.00	.....	.....	.....	.....	.....	.....

TABLE 4

*Total losses and gains of the sand, silt, and clay in different horizons of Dayton silt loam*

HORIZON	VOLUME FACTOR*	LOSS OR GAIN OF SAND		LOSS OR GAIN OF SILT		LOSS OR GAIN OF CLAY		NET LOSS OR GAIN PER COLUMN Z
		Per 100 gm. of parent material	Per column Z	Per 100 gm. of parent material	Per column Z	Per 100 gm. of parent material	Per column Z	
		gm.	gm.	gm.	gm.	gm.	gm.	gm.
A <sub>1</sub> .....	2.3	+1.15	+2.64	-3.74	-8.60	-11.49	-26.43	
A <sub>2</sub> .....	9.1	+1.13	+10.28	-5.08	-46.23	-8.35	-75.98	
A <sub>2</sub> -B.....	4.5	+2.00	+9.00	-11.82	-53.19	-0.84	-3.78	
Total per column Za.....	15.9	.....	+21.92	.....	-108.02	.....	-106.19	-192.29
B.....	11.8	+0.44	+5.19	-25.35	-299.13	+26.45	+312.11	
B-C.....	8.0	-0.68	-5.44	-14.65	-117.20	+16.60	+132.80	
Total per column Zb.....	19.8	.....	-0.25	.....	-416.33	.....	+444.91	+28.33

\* The present thickness of the horizon corrected according to the parent material quotient.

of various clay materials was leached to the amount of about 160 gm. per column Zb. The evidence of this process will be brought out in the following pages.

#### *Chemical composition*

Table 5 gives the data on chemical composition of the whole soil in the principal horizons of Dayton silt loam. As has been pointed out, data like those in

table 5 show only apparent changes in composition of the original material in different horizons, and the true losses and gains of various constituents in these horizons can be shown only by recalculating these data on a certain constant factor.

There are several reasons to believe that silica in the Dayton soil is the least likely to be moved from one horizon into another, although it may undergo certain changes in mode of combination. It is true that there is no absolute proof of its stability and that the evidence of its immobility is rather circumstantial. The distinctly acid reaction throughout the A horizon (pH 4.8) prevents dissolution of silica and stimulates the migration of the sesquioxides. Thus, the relative increase of silica in the A horizon in respect to its content in the C most likely is due to the leaching of sesquioxides and other constituents such as lime and magnesia.

TABLE 5

*Chemical composition of the whole soil material in different horizons of Dayton silt loam*  
Calculated on basis of soil free of organic matter and combined water

	A <sub>1</sub>	A <sub>2</sub>	A <sub>2</sub> -B	B	B-C	C
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
SiO <sub>2</sub> .....	76.16	74.63	73.24	64.44	64.62	65.44
Al <sub>2</sub> O <sub>3</sub> .....	13.16	13.93	14.90	19.32	18.25	18.06
Fe <sub>2</sub> O <sub>3</sub> .....	3.81	4.47	5.00	8.92	8.59	7.31
CaO.....	0.98	0.98	0.93	1.48	2.10	2.18
MgO.....	0.84	0.91	1.08	1.97	2.14	2.13
K <sub>2</sub> O.....	2.22	2.27	2.08	1.43	1.53	1.92
Na <sub>2</sub> O.....	1.26	1.33	1.28	0.90	1.15	1.30
MnO.....	0.08	0.06	0.08	0.16	0.13	0.14
TiO <sub>2</sub> .....	1.29	1.31	1.32	1.32	1.31	1.26
P <sub>2</sub> O <sub>5</sub> .....	0.20	0.11	0.09	0.06	0.18	0.26
pH.....	4.8	4.8	4.8	6.3	7.2	7.0

A rather sharp change of reaction at the boundary between the A and B horizons from pH 4.8 to pH 6.3 might be the cause of the precipitation of sesquioxides in the B, leading to a slight relative decrease in silica in this horizon. The A horizon is thoroughly pervaded by abundant podzolic flour, which probably represents a residue of highly siliceous material. Most likely, it is fine silt and coarse clay stripped of iron and manganese oxides and other coloring constituents. Whatever its origin or character, however, the mere presence of the podzolic flour is an indication that silica, or at least a highly siliceous material, remains in place, whereas the other constituents move out.

A greater content of silica in the A in comparison with that in the B and C could hardly be attributed to a stronger leaching of the lower horizons, because such an explanation would lead to the wholly untenable assumption that the C horizon is affected by leaching to a greater extent than the A.

We are fully aware that this reasoning does not prove the absolute immobility of silica throughout the profile of Dayton silt loam. We assume, however, that

the changes in content of silica in different horizons must be rather insignificant as compared with those of various other constituents and that the losses and gains of these constituents calculated in respect to silica are not very far from the true losses and gains. On the assumption of relative stability of silica, the

TABLE 6

*Content of various constituents in the gram-equivalents of the soil in different horizons of Dayton silt loam and relative losses and gains of these constituents in respect to silica*

	CONTENT PER GRAM-EQUIVALENT OF THE SOIL						LOSS OR GAIN PER 100 GM. OF PARENT MATERIAL				
	A <sub>1</sub>	A <sub>2</sub>	A <sub>2</sub> -B	B	B-C	C	A <sub>1</sub>	A <sub>2</sub>	A <sub>2</sub> -B	B	B-C
	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.
SiO <sub>2</sub> .....	65.44	65.44	65.44	65.44	65.44	65.44	.....	.....	.....	.....	.....
Al <sub>2</sub> O <sub>3</sub> .....	11.31	12.22	13.31	19.62	18.48	18.06	-6.75	-5.84	-4.75	+1.56	+0.42
Fe <sub>2</sub> O <sub>3</sub> .....	3.27	3.92	4.47	9.06	8.70	7.31	-4.04	-3.39	-2.84	+1.75	+1.39
CaO.....	0.84	0.86	0.83	1.50	2.13	2.18	-1.34	-1.32	-1.35	-0.68	-0.05
MgO.....	0.72	0.80	0.96	2.00	2.17	2.13	-1.41	-1.33	-1.17	-0.13	+0.04
K <sub>2</sub> O.....	1.91	1.99	1.86	1.45	1.55	1.92	-0.01	+0.07	-0.06	-0.47	-0.37
Na <sub>2</sub> O.....	1.08	1.17	1.14	0.91	1.16	1.30	-0.22	-0.13	-0.18	-0.39	-0.14
MnO.....	0.07	0.05	0.07	0.16	0.13	0.14	-0.07	-0.09	-0.07	+0.02	-0.01
TiO <sub>2</sub> .....	1.11	1.15	1.18	1.34	1.33	1.26	-0.15	-0.11	-0.08	+0.08	+0.07
P <sub>2</sub> O <sub>5</sub> .....	0.17	0.10	0.08	0.06	0.18	0.26	-0.09	-0.16	-0.18	-0.20	-0.08
Total...	85.92	87.70	89.34	101.54	101.27	100.00	-14.08	-12.30	-10.66	+1.54	+1.27

TABLE 7

*Total losses and gains of various constituents in different horizons of Dayton silt loam*

HORIZON	VOLUME FACTOR*	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	OTHER ELEMENTS (NET)	NET LOSS OR GAIN PER COLUMN Z
		gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.
A <sub>1</sub> .....	2.3	-16	-9	-3	-3	?	?	?	
A <sub>2</sub> .....	9.1	-53	-31	-12	-12	?	?	?	
A <sub>2</sub> -B.....	4.5	-21	-13	-6	-5	?	?	?	
Total per column Za.....	15.9	-90	-53	-21	-20	?	?	about -8	about -192
B.....	11.8	+18	+21	-8	-2	-6	-5	?	
B-C.....	8.0	+3	+11	....	....	-3	-1	?	
Total per column Zb.....	19.8	+21	+32	-8	-2	-9	-6	?	about +28

\* The present thickness of the horizon corrected according to the parent material quotient.

data given in table 5 are recalculated upon the parent material quotient and again upon the volume factor. As the constant factor (*K*), 65.44 gm. of silica, which is present in 100 gm. of the presumably unmodified parent material, is assumed. The results of these calculations are presented in tables 6 and 7.

The derived data in table 6 are expressed in grams per 100 gm. of the original material, and those in table 7, in grams per column Z extending throughout the corresponding horizon. The relative losses and gains are determined by the difference between the content of any constituent in 100 gm. of the parent material and in the equivalent amount of the modified material in a given soil horizon. The total losses and gains shown in table 7, are only roughly approximate. Estimates of losses and gains of the minor elements with such an approximation are not trustworthy, and, therefore these data are not included in table 7.

*Migration of the sesquioxides.* The data in table 7, show that about 31 per cent of the alumina and about 46 per cent of the iron oxide<sup>5</sup> have been leached from the A horizon, including A<sub>1</sub>, A<sub>2</sub>, and A<sub>2</sub>-B. About 23 per cent of the alumina and about 60 per cent of the iron oxide which were leached from the A are retained in the B horizon. The remaining 77 per cent of alumina which was released in the A apparently is leached entirely from the soil profile. The fate of the remaining 40 per cent, or about 21 gm. per column Za, of iron oxide is less certain. Most likely this amount of liberated iron was not shifted from the A horizon but was segregated in the large iron-manganese concretions which were not included in the soil sample taken for analysis because particles larger than 2 mm. diameter are discarded in the routine preparation of samples for analysis. The data given by Drosdoff and Nikiforoff (5) on the iron content of the large concretions in this soil tend to support this view.

The differences in percentage of the total alumina and iron oxide that was leached from the A and in percentage of the migrant alumina and iron oxide that was retained in the B, coupled with the difference in the fate of the remaining parts of liberated alumina and iron suggest that the sesquioxides migrate from the A horizon into the B and farther down independently of each other in a free state. No determination of free alumina was made, but 1.10 per cent of free iron oxide has been found in the A and 0.80 per cent in the B (in percentage of the whole soil). The content of total iron in the A<sub>2</sub> and B is 3.92 and 9.06 per cent, respectively which indicates that about 28 per cent of the total iron in the A<sub>2</sub> horizon is in the form of free oxide, whereas in the B only about 9 per cent is free. Perhaps, the difference in percentages of free iron in these horizons is due to the fact that the A<sub>2</sub> horizon is a zone of release, whereas the B horizon is a zone of secondary fixation of iron in which the isomorphous replacement may play an important part.

<sup>5</sup> The formula employed in calculating the percentages is as follows:

$$x = \frac{100 \cdot R}{v \cdot A}$$

in which  $x$  is the total loss or gain of a given substance in percentage of the total amount of this substance in the  $v$  100 gm. of parent material;  $R$  is the total loss or gain of this substance in a given soil horizon;  $v$  is the volume factor of this horizon; and  $A$  is the amount of the same substance in 100 gm. of the parent material (percentage). For example, if 100 gm. of parent material contains 18.06 gm. of alumina and if the volume factor of the A horizon is 15.8, then the original content of alumina in column Za was  $15.8 \times 18.06$ , or about 285 gm. The total loss of alumina from such a column is about 90 gm., which makes up about 31 per cent of the original amount.

The combined loss of sesquioxides in the A horizon is about 143 gm. per column Za, whereas the loss of clay from such a column, as shown by mechanical analysis, amounts to about 100 gm. It may be assumed, therefore, that the release of free sesquioxides in the A depends in part upon the decomposition of the material coarser than clay, especially of silt. The combined gain of sesquioxides in the B is about 53 gm. per column Zb, whereas the gain of clay in this column is about 450 gm. Thus, the sesquioxides which were transferred from the A into the B constitute only about 12 per cent of the increase in the content of clay in the B.

*Migration of lime and magnesia.* The data in table 7 show that about 60 per cent of the total lime and magnesia was leached from the A horizon. Unlike the sesquioxides, neither lime nor magnesia that was leached from the A is retained in the B. To the contrary, leaching of lime continues throughout the B, although to a lesser extent than in the A. The leaching of magnesia from the B is not certain. The leaching of both lime and magnesia ceases in the lowermost part of B, i.e., in the B-C horizon.

The amounts of lime and magnesia which were leached from different horizons do not represent the extent of the decomposition of the minerals that carry these bases. A relatively large part of the released calcium and magnesium is retained in the soil in exchangeable form. As will be shown in part II,<sup>6</sup> a large part of the calcium still present in certain horizons of this soil is in the exchangeable form with little combined calcium left. Considerably less exchangeable magnesium has been found, and the greater part of the magnesium left is in the combined form. It is probable, however, that the primary magnesium minerals have decomposed, releasing magnesia, which has recombined with silica and alumina to form the secondary clay minerals.

*Migration of the alkali bases.* The data in table 7 show that, unlike the lime and magnesia, the soda and potash are leached from the B horizon to a greater extent than from the A. As a matter of fact, these data show no leaching of potash and the removal of a very small and uncertain amount of soda from the A horizon, whereas about 23 per cent of these oxides were leached from the B. The released soda and potash, like most of the released lime and magnesia, are leached entirely from the soil profile. Analysis of the exchangeable bases shows a very small amount of the exchangeable sodium and potassium (table 4, part II).<sup>6</sup> Thus, it may be assumed that almost all potash and soda left in the soil is in the combined form.

These data indicate that in the A horizon the soda and especially the potash minerals are relatively more stable than the lime and magnesia minerals, whereas in the B horizon the behavior of these two groups of minerals tends to be reversed, which suggests a certain qualitative difference between the processes which control the development of the A and B horizons respectively.

*Migration of the minor elements.* A loss of about 50 per cent of manganese in the A horizon is significant. Such a loss, however, most likely is due to the segregation of manganese in the large iron-manganese concretions rather than

<sup>6</sup> Nikiforoff, C. C., and Drosdoff, M. Genesis of a claypan soil: II. *Soil Sci.* (in press).

to the migration of manganese. There is a probability of migration from the A into the B horizon of a rather small part of titania and also of the loss of phosphorus in both A and B horizons.

*Summary on migration.*—The A horizon including the A<sub>1</sub>, A<sub>2</sub>, and A<sub>2</sub>-B of Dayton silt loam has lost through leaching about one third of the alumina, about one half of the iron oxide, about two thirds of the lime and magnesia, and probably some parts of soda, titania, and phosphorus. The combined loss of all constituents amounted to about 192 gm. per column Za, which had an initial weight of about 1,590 gm. Thus, the total loss due to leaching amounted to about 12 per cent by weight of the original material. This loss caused a relative increase in content of silica in the residue from 65.44 to about 74.6 per cent.

The mechanical analysis showed that about half of the combined total loss in the A horizon was from the clay and the other half from the silt. A small decrease in content of silt and clay in the A was due to the formation of concretions.

Less than one third of the alumina and about two thirds of the iron oxide which were shifted from the A were retained in the B. The remaining iron oxide and very likely all the manganese oxide lost in the A were segregated in the iron-manganese concretions. The remaining part of the alumina as well as all the lime and magnesia were leached entirely from the solum. Leaching of lime continued throughout the B. Leaching of the alkali bases from the A is uncertain, whereas the B lost about one fourth of these bases.

Only about one fourth of the material that was moved out from the A was retained in the B, whereas the other three fourths were leached entirely from the soil together with a small amount of material lost by the B itself. Thus, the material that was shifted from the A into the B made up only a small part of the increase in content of clay in the B horizon.

Most of the clay which accumulated in the B was formed in place by the decomposition of silt. It follows that migration was relatively unimportant for the formation of the claypan. The details of the formation of the clay in place are discussed in part II of this paper.<sup>6</sup>

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